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Nonequilibrium thermodynamics of interacting tunneling transport: variational grand potential, density functional formulation and nature of steady-state forces

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Abstract

The standard formulation of tunneling transport rests on an open-boundary modeling. There, conserving approximations to nonequilibrium Green function or quantum statistical mechanics provide consistent but computationally costly approaches; alternatively, the use of density-dependent ballistic-transport calculations (e.g., Lang 1995 *Phys. Rev. B* **52** 5335), here denoted ‘DBT’, provides computationally efficient (approximate) atomistic characterizations of the electron behavior but has until now lacked a formal justification. This paper presents an exact, variational nonequilibrium thermodynamic theory for fully interacting tunneling and provides a rigorous foundation for frozen-nuclei DBT calculations as a lowest-order approximation to an exact nonequilibrium thermodynamic density functional evaluation. The theory starts from the complete electron nonequilibrium quantum statistical mechanics and I identify the operator for the nonequilibrium Gibbs free energy which, generally, must be treated as an implicit solution of the fully interacting many-body dynamics. I demonstrate a minimal property of a functional for the nonequilibrium thermodynamic grand potential which thus uniquely identifies the solution as the exact nonequilibrium density matrix. I also show that the uniqueness-of-density proof from a closely related Lippmann–Schwinger collision density functional theory (Hyldgaard 2008 *Phys. Rev. B* **78** 165109) makes it possible to express the variational nonequilibrium thermodynamic description as a single-particle formulation based on universal electron-density functionals; the full nonequilibrium single-particle formulation improves the DBT method, for example, by a more refined account of Gibbs free energy effects. I illustrate a formal evaluation of the zero-temperature thermodynamic grand potential value which I find is closely related to the variation in the scattering phase shifts and hence to Friedel density oscillations. This paper also discusses the difference between the here-presented exact thermodynamic forces and the often-used electrostatic forces. Finally the paper documents an inherent adiabatic nature of the thermodynamic forces and observes that these are suited for a nonequilibrium implementation of the Born–Oppenheimer approximation.

(Some figures may appear in colour only in the online journal)

1. Introduction

An understanding of self-organizing functional molecular systems is a challenge for condensed matter physics theory. Molecular self-assembly mechanisms [1–4]¹ provide a

low-cost fabrication approach² which mimics the molecular-recognition principle [7] of Nature. The approach can open technological possibilities, for example, atomically precise production of electronics [8] and switching [9] components. The functionality is specified by the quantum-mechanical

¹ An example of a van der Waals interaction study for larger-scale molecular-overlayer assembly is included in [5].

² For example, based on DNA sequencing that programs and controls three-dimensional organization of DNA-coated gold nanoparticles [6].

behavior of the electrons which typically respond to nonequilibrium conditions. It is natural to assume a Born–Oppenheimer approximation of sorts and solve the nonequilibrium electron dynamics problem for model systems or for frozen-nuclei coordinates within systematic approximations to the electron quantum-kinetic account (QKA)³ [10–18].

Electron QKA methods range from time-evolution formulations^{4,5}, exact reformulations (here termed ReNQSM) of the nonequilibrium quantum statistical mechanics for tunneling [18, 21] (including formal [22–26], time-averaged [27], and variational [28] approaches), over constrained entropy maximization descriptions [29–31], and to conserving nonequilibrium Green function approximations [12, 14–16, 32–35]. In the context of nanoscale tunneling transport, there exist, for example, formal generalizations [36–38] of the Landauer–Büttiker formula [39]⁶ to problems with many-body interaction, but also warnings [21, 37, 41–44] of a breakdown for an oversimplified single-particle (SP) interpretation of this formal result. The electron QKA furthermore includes Wigner distribution calculations, for example, as described in an early and clear discussion [45] of the role of open boundaries and of a need for a thermodynamical treatment of nonequilibrium tunneling. The grand canonical-ensemble (GCE) thermodynamics foundation is essential to correctly handle all charging [42, 46] (and hence Gibbs free energy) effects, spontaneous- and stimulated-emission effects [47], the nonequilibrium entropy production [48] and the entropy-transport effects [49] in a tunneling structure connecting leads at different chemical potentials.

Electron QKA studies have, until recently, delayed the discussion of the nonequilibrium forces which are exerted on the nuclei by transport-induced changes in the electron behavior. Nevertheless, the frozen-nuclei (i.e., electron) QKA methods are, by themselves, still empirical in the sense that they depend on an *a priori* characterization of the material’s structure. This is a limitation since it is a central result from the family of electron-density functional theory (DFT) formulations [50–64] that the electron behavior is uniquely determined by the specific atomic configuration. Also, molecular systems are characterized by sparseness [65], i.e., have regions of low electron concentrations where

dispersive forces act and where the system components are relatively free to adapt their morphology to the specific (transport-dependent) environment. To guide development of a molecular system to a pre-specified functionality, we must develop a nonempirical theory of nonequilibrium interaction effects [22, 23, 25, 26, 28, 37, 41, 42, 45, 66–85], and structural relaxations/excitations [86–110] in nanoscale transport.

Traditional, that is, ground-state DFT [50, 51] illustrates the level of detail and predictive power that we desire from a new nonempirical yet efficient nonequilibrium computational theory of interacting tunneling. Ground-state DFT rests on an equilibrium (canonical-ensemble) total-energy variational principle and regularly delivers accurate characterizations of both the electron and atomic structure for dense (hard) matter problems when using a generalized gradient approximation [111] for the electron-density functional. With the introduction of truly nonlocal functionals like the van der Waals density functional method [112, 113] or other formulations [114] it has become possible to extend the reach of nonempirical ground-state DFT also to the broader class of sparse matter [65, 115] (including molecular structures and devices) in equilibrium. These developments come in addition to many versatile (but not entirely nonempirical) ground-state DFT extensions [116]. The parameter-free DFT characterization of, for example, molecular-system structure, is possible because ground-state DFT determines adiabatic forces which guide relaxations to an optimal atomic configuration. However, it is essential to point out that the desired nonempirical theory for nonequilibrium tunneling must involve a significant step beyond ground-state DFT; the nonequilibrium operating conditions void the ground-state DFT variational principle and the current flow causes the equilibrium Born–Oppenheimer-approximation concepts⁷ (system staying in the evolving ground state while being thermally isolated, free of charging) to lose meaning.

The GCE modeling framework of tunneling is fully incorporated in the density-dependent ballistic-transport method [118–122] (here termed DBT) inspired by the Landauer–Büttiker formula [39]. This method utilizes the density functionals of ground-state DFT to define an effective (density-dependent) potential for elastic scattering; it also solves for the density, formally through use of the SP Lippmann–Schwinger (LS) equation [118, 123, 124]. I note that this DBT approach delivers computationally efficient, parameter-free (but approximate) system-specific characterizations of the electron behavior. However, the DBT method has had no real status as a nonempirical theory because it has had no rigorous foundation.

The QKA delivers a full GCE thermodynamic description [11, 13, 15, 16, 18, 45] which is inherently exact. It is natural to seek a QKA recast and thus enable exact nonempirical characterizations of both electron behavior and nuclei relaxations (specified by the thermodynamic forces of the exact electron QKA). Access to efficient computations

³ The present paper benefits from connecting to several different formulations of the quantum physical behavior of electrons and must relate to many concepts. The use of abbreviations has been restricted to terms that are both long and used frequently or that enter as labels in equations and may assist an identification of the nature of the implied evaluation. The abbreviations are, in alphabetical order, as follows: DBT—density-dependent ballistic transport, calculated from the effective potential of ground-state DFT and assuming independent transmission; DFT—density functional theory; GCE—grand canonical ensemble; LS—Lippmann–Schwinger; MSS—metallic surface state; ReNQSM—exact reformulation of nonequilibrium quantum statistical mechanics; QKA—quantum-kinetic account; SP—single-particle.

⁴ For formulations based on renormalization group theory, see, for example, [19].

⁵ For formulations based on the Lindblad functional see, for example, [20].

⁶ For a corresponding wavefunction analysis of noninteracting tunneling, please see [40].

⁷ A general, concept-based (as opposed to operational) description of an assumed adiabatic nature is given in [117].

of the exact thermodynamics of interacting nonequilibrium tunneling would refine the description of the coupling between charge-transfer processes and molecular assembly and structure. It would also deepen the understanding of defect-induced local-density-of-state changes measured by scanning-tunneling microscopy [1, 2, 125, 126], of inelastic tunneling microscopy [94, 95, 127], of current-induced catalytic processes [88], of the current-induced nanopipette effect⁸, of current-induced phonon generation [96, 101, 102, 109] light emission and lasing [47]⁹, as well as of molecular switching and memristor effects [8, 9]. Furthermore, from an understanding of the exact nonequilibrium thermodynamics we can discuss a nonequilibrium Born–Oppenheimer approximation for a strictly electron QKA of morphology relaxations in working nonequilibrium tunneling systems (thus supplementing a recent analysis for tunneling with an electron–phonon coupling [109]). This is because we can identify the nonequilibrium adiabatic nature [117] of infinitely slow relaxations that both ensures an automatic compliance with the Friedel sum rule [130] (and hence charge adjustments [42] that lead to important Gibbs free energy effects) and avoids creation of an under-relaxed entropy content.

This paper reformulates the electron QKA of nonequilibrium quantum statistical mechanics of interacting tunneling and thus (a) derives an exact variational GCE formulation of the nonequilibrium thermodynamics. The paper furthermore (b) expresses the thermodynamics as a regular DFT and, for steady-state problems, (c) identifies universal density functionals permitting a rigorous SP formulation. The paper thus (d) establishes the widely used but previously *ad hoc* DBT method for frozen-nuclei–electron density calculations as a lowest order yet consistent approximation. Moreover, the paper (e) shows that the variational property of the thermodynamic potential reflects a maximization of entropy subject to an automatic and rigorous implementation of boundary conditions. The author is not aware of any previous derivations of the DBT method as a rigorous nonempirical theory. In any case, the here-presented derivation of an SP framework for efficient DFT calculations of nonequilibrium thermodynamics is useful as it opens the way to systematic improvements of the DBT method by identifying the nature of a set of transport-relevant, exact, universal density functionals. These universal functionals govern the nonequilibrium internal energy exchange and correlation and the Gibbs free energy effects.

The nonequilibrium thermodynamic functional theory is a generalization of Mermin’s equilibrium thermodynamic theory [52] and takes off from the exact ReNQSM descriptions [21, 23, 25, 26, 73, 74, 131]. In this paper I motivate and provide a definition of an exact nonequilibrium thermodynamic grand potential value and a corresponding

functional,

$$\Omega_{\text{col}}(t) \equiv -\frac{1}{\beta} \ln \text{Tr}\{e^{-\beta[H(t) - \hat{Y}_{\text{col}}(t)]}\}, \quad (1)$$

$$\Omega_{\text{col}}[\hat{\rho}(t)] \equiv \text{Tr}\{\hat{\rho}(t)[H(t) - \hat{Y}_{\text{col}}(t) + \beta^{-1} \ln \hat{\rho}(t)]\}, \quad (2)$$

respectively. Here, $H(t)$ denotes a general time-dependent Hamiltonian and β is the inverse temperature. The definition and formal results are made possible by the identification of an operator $\hat{Y}_{\text{col}}(t)$ for the nonequilibrium Gibbs free energy. The Gibbs free energy operator is in general emerging, that is, implicitly defined and given through an operator description of the interacting many-body time evolution. The nonequilibrium thermodynamic grand potential (2) is a functional of the class of possible nonequilibrium (time-dependent) density matrices $\hat{\rho}(t)$. The subscripts ‘col’ (used for general time-dependent tunneling cases) on thermodynamics operators and values, e.g. in equation (2), emphasize that the nonequilibrium interaction problem is solved as a formal many-body collision problem. That is, it is expressed in the framework of general collision theory [123, 132–138], an approach that was also taken in a recent (related) formulation of an LS-based collision theory DFT, below identified as ‘LS collision DFT’ [64]. The here-presented exact nonequilibrium thermodynamic theory rests on a continuum Caroli partition scheme [32, 33] and it is therefore possible to discuss the formal nature of forces on nuclei¹⁰.

In steady state the nonequilibrium thermodynamic solutions are given by the many-body LS solutions [123, 138] $|\Psi_{\xi}^{(+)}\rangle$ which are projections [134] of the full time evolution of initial states $|\Phi_{\xi}\rangle$. However, while $|\Phi_{\xi}\rangle$ is an eigenstate of energy E_{ξ} of $H(t \rightarrow -\infty)$, the many-body LS solution (generally) describes evolution at a different energy, $E_{\xi} + \Delta_{\xi}$, with shifts Δ_{ξ} specified from the T -matrix behavior or by the self-energy [133–135]. The references [136] and [137]

¹⁰There do not seem to be many prior nonequilibrium thermodynamic investigations of the nature of forces in the strictly adiabatic limit, when the mass of the electrons is taken to be infinitely smaller than that of the ions. The reference [98] lists two interesting thermodynamic investigations of the nature of forces, for example, in linear response. Both are limited to a study of noninteracting particles and build from a ground-state DFT characterization and analysis of left- (‘1’) and right-moving (‘2’) states by thermodynamic arguments. The starting point assumes that two chemical potentials $\mu_{i=1,2}$ ensure given electron occupations N_1 and N_2 of these different classes of states. At fixed N_1 and N_2 , one has a canonical-ensemble description and the forces are then electrostatic in nature and given by the traditional Hellmann–Feynman theorem. For an open system, the papers observe that $\delta U = \sum_i \mu_i \delta N_i$ provides the correct GCE link between relevant extensive quantities (here given in the absence of entropic effects). The papers proceed by adding an electrostatic force work term $\delta W^{\text{es}} \equiv \mathbf{F}_{\mathbf{R}_i}^{\text{es, NEQ}} \delta \mathbf{R}_i$ when characterizing the added effects of an infinitesimal coordinate change. However, for any given value of the occupation changes $\delta N_{1,2}$, a coordinate change must (by the Friedel sum rule) cause concerted changes in both the internal energy and the chemical potentials. Also, in a GCE thermodynamic system one cannot assume a thermally isolated behavior and the correct determination of the work δW must therefore equate changes in both the internal energy and the heat δQ , that is, $\delta W = \delta U + \delta Q$. The papers listed in [98] cannot be viewed as a conclusive thermodynamic analysis of forces in nonequilibrium tunneling because they do not state an argument that a GCE evaluation of electrostatic forces (6) will capture all heat effects, including all nonequilibrium charging and all electron redistribution mechanisms [21].

⁸ The nanopipette is an explicit demonstration (by *in situ* experiments) that electron currents cause matter transport in a nanoscale system, [128].

⁹ For an example theory study discussing a significant bias-induced enhancement of electron–electron scattering in a resonant tunneling quantum-cascade-laser [47] system, please see [129].

give example usage of the formal many-body LS solution in condensed matter physics problems. We can choose the initial states to also be eigenstates Y_ξ of the initial Gibbs free energy $\hat{Y}_d = \hat{Y}_{col}(t \rightarrow -\infty)$. In steady state the many-body LS solutions thus define a formal evaluation of the nonequilibrium density matrix

$$\hat{\rho}_{LS} \equiv \sum_{\xi} |\Psi_{\xi}^{(+)}\rangle \exp[-\beta(E_{\xi} + \Delta_{\xi} - Y_{\xi})] \langle \Psi_{\xi}^{(+)}|. \quad (3)$$

In such steady-state problems, the operator for the nonequilibrium Gibbs free energy $\hat{Y}_{col}(t)$ becomes identical to the electron redistribution operator ‘Y’ of the steady-state ReNQSM [21]. Below, I identify steady-state thermodynamic operators and values by subscripts ‘LS’ to emphasize the direct link to the many-body LS solution.

The demonstration of an extremal nature of $\Omega_{LS}[\hat{\rho}] > \Omega_{LS}[\hat{\rho}_{LS}]$ leads to additional formal and rigorous results. The foundation of the electron QKA ensures that the here-presented thermodynamic theory contains all boundary, entropy and entropy-flow effects in the electron system. The paper therefore (f) provides an exact demonstration that the thermodynamic forces

$$\mathbf{F}_{LS, \mathbf{R}_i}^{GCE} \equiv -\frac{\partial}{\partial \mathbf{R}_i} \bar{\Omega}_{LS} \quad (4)$$

are explicitly conservative and specified by a here-demonstrated generalized Hellmann–Feynman theorem,

$$\frac{\partial}{\partial \mathbf{R}_i} \bar{\Omega}_{LS} = \left\langle \frac{\partial}{\partial \mathbf{R}_i} [H - \hat{Y}_{LS}] \right\rangle_{\hat{\rho}_{LS}}. \quad (5)$$

These thermodynamic forces are formally different from the (nonequilibrium, identified by ‘NEQ’) electrostatic force definition,

$$\mathbf{F}_{\mathbf{R}_i}^{es, NEQ} \equiv -\left\langle \frac{\partial H}{\partial \mathbf{R}_i} \right\rangle_{NEQ \text{ GCE}}, \quad (6)$$

which has gained usage in GCE modeling, for example, as exploited for relaxations in DBT implementations¹¹ [139, 140].

There exist arguments for use of electrostatic forces in linear response, for example, as summarized in [87] and [98]. However, there is no rigorous argument¹² for the general use of electrostatic forces (6) in infinite, open nonequilibrium tunneling systems. I demonstrate that the electrostatic forces (6) do agree with the exact thermodynamic forces (4) when the electron distribution can be entirely described from the full density of states. At the same time, I observe that the latter is not generally a correct assumption under nonequilibrium conditions. In any case, the paper (g)

represents a rigorous QKA demonstration that electrostatic forces (6) with a nonconservative character [106, 107] can never agree with the steady-state thermodynamic forces (4).

I stress that the here-derived steady-state thermodynamic forces (4) are useful as they define an adiabatic nature of relaxations. A sufficiently slow implementation of the exact thermodynamic forces (4) ensures that the nonequilibrium system will emerge with a correct and extremal steady-state thermodynamic potential value. The paper thereby (h) demonstrates that the resulting system must be described by the uniquely defined nonequilibrium density matrix $\hat{\rho} = \hat{\rho}_{LS}$ that represents the steady-state solution for the system (Hamiltonian) after the coordinate translation. A slow deformation around any closed loop can never produce any change in any thermodynamic quantity. The paper (i) shows that the thermodynamic forces (4) ensure a correct Gibbs free energy content and always avoid an under-relaxed entropy content. The conservative thermodynamic forces express a robust physical principle, namely entropy optimization tempered by an automatic implementation of rigorous nonequilibrium GCE boundary conditions. In essence, the paper (j) suggests that the exact thermodynamic forces (4) are suited for use in a nonequilibrium Born–Oppenheimer approximation for steady-state tunneling described as an open-boundary GCE system.

While the set of formal results, (a) through (j), represents the main contribution, the paper also summarizes an SP framework for computing the zero-temperature variation of the exact thermodynamic grand potential $\Delta\Omega_{LS}$. This is relevant for completing a nonempirical characterization of nonequilibrium tunneling systems and, for example, describing the transport which emerges after (adiabatic) relaxation of the morphology. Since the paper constitutes a rigorous DFT formulation of nonequilibrium thermodynamics, it is sufficient to consider an evaluation of the thermodynamic variation for noninteracting particles. Robust computational schemes [118–122] already exist and provide SP LS solutions, i.e., the noninteracting scattering states. Previous determinations of nonequilibrium thermodynamical forces have often focused on the real-space variation of such scattering states, making it important to ensure consistency in the limiting processes [98, 134, 135]. Noting that the SP LS solutions are local in wavevector space, I summarize an alternative formal approach defined by the *S*-matrix formulation [142] of the generalized Friedel sum rule [130, 137, 143] and emphasizing computations of the phase-shift variation [144–147]. The formal framework attempts to utilize the availability of DBT solvers and their description of scattering phase shifts. It may well be possible to also develop alternative, perhaps more robust and efficient, computation strategies.

The paper is organized as follows. Section 2 summarizes computations of the noninteracting thermodynamic grand potential variation, emphasizing the key role of the Gibbs free energy in GCE thermodynamic problems. Section 3 defines the partition scheme while section 4 presents the electron QKA and the exact reformulation as a variational nonequilibrium thermodynamic theory. Section 5 presents

¹¹ Both [139] and [140] report calculations as well as details of efficient code implementations of an approximative nonempirical description of tunneling (including current-induced relaxations) based on use of electrostatic forces. This electrostatic force evaluation is given by the density variation as can be calculated in the DBT method [118–122].

¹² The use of electrostatic forces (6) is sometimes motivated by a referral to Ehrenfest theorem [141]. Section 9 explains limitations, also pointed out in [97], that prevent that approach from always giving a conclusive argument in an open system.

the set of general nonequilibrium GCE thermodynamic results for steady-state tunneling while section 6 defines and discusses state functions and forces for steady-state tunneling. The linking with LS collision DFT [64] and the SP formulation as a thermodynamic DFT is presented in section 7 while section 8 outlines an SP framework for calculating the zero-temperature thermodynamic variation. Section 9 contains a discussion, while section 10 contains a summary and conclusions. In addition, the paper has five appendices, introduced in and supporting the text.

2. Open-boundary thermodynamics of noninteracting particles

The paper begins by summarizing a general framework for calculating the noninteracting GCE thermodynamic variation with illustrations of the key role held by the Friedel sum rule in specifying, for example, the Gibbs free energy variation. The section presents a nonequilibrium thermodynamic formulation given in terms of the nonequilibrium Green function techniques [148]. I detail the relation to formal scattering theory through a recast that emphasizes the independent-particle nature of the associated S -matrix [143, 146, 147, 149, 150]. An analysis of the formal S -matrix behavior is also exploited in [109]. A summary and presentation is given to illustrate the feasibility of such calculations and because textbooks on thermodynamic calculations tend to rapidly proceed to the more difficult problem of investigating the effects of an actual many-body interaction. The latter is something that this paper instead proposes to (eventually) handle through a rigorous DFT SP formulation (given also developments of the nonequilibrium density functionals). The Gibbs free energy is essential in GCE thermodynamic studies due to the possibility and necessity of open-infinite systems to accommodate charge adjustments [130, 143].

The presentation is supported by appendix A, which summarizes a Green function thermodynamics description [148], and appendix B, which details the S -matrix, Friedel sum rule [143] and scattering phase-shift analysis [144, 145]. The formal framework is presented with the intention to explore (in later works) the existence of efficient SP LS solvers, an integral part of the DBT codes [118–122], for thermodynamics calculations.

2.1. Friedel sum rule, phase shifts, and thermodynamics

With a GCE description of the electron system, there are typically charge transfers and associated thermodynamic effects that significantly influence the interactions of classical particles (e.g., defects or nuclei immersed in the electron gas). The charge adjustments are in the GCE specified by the Friedel sum rule [130, 137, 143], expressed as an integrated change in the density of state, and thus a direct cause for changes in the Gibbs free energy. This is true in equilibrium and out of equilibrium.

A natural starting point for a discussion of noninteracting tunneling thermodynamics is the general formulation of the Friedel sum rule [143],

$$\Delta\mathcal{N}(\mu') = \frac{1}{2i\pi} \text{Tr}\{\ln[S(\mu')]\}. \quad (7)$$

The sum rule is here expressed as a relation between the scattering (or S) matrix $S(\mu)$ for single-particle excitations at a given chemical potential μ' and the total number of displaced electrons, $\mathcal{N}(\mu')$. The trace includes a factor of 2 for spin; I shall, for simplicity, assume spin degeneracy and restrict the summation over SP states to per-spin representation. I shall also, in this section, focus exclusively on a zero-temperature formulation. In a central potential, the eigenstates of the S -matrix are just $\exp[2i\delta_{l,m}(\omega)]$ and the traditional Friedel sum rule [130] follows simply from an evaluation of the trace of the logarithm in the powerful generalization (7). The sole condition for the derivation [143] of (7) is that the imaginary part of the many-body self-energy vanishes, $\text{Im}\Sigma_{\mu'} = 0$. This is true at the actual Fermi level $\mu' = \mu_F$ even for an interacting equilibrium many-body system.

References [149, 150] provide early examples of a broader usage of (7) for DFT-based interaction studies, namely in elegant SP LS studies of the adsorbate-induced density of state changes $\Delta\mathcal{D}(\omega)$. Formally one seeks the adsorption-induced changes in the density of states,

$$\Delta\mathcal{D}(\omega) \equiv 2 \sum_{\lambda} \{\delta(\omega - \tilde{\epsilon}_{\lambda}) - \delta(\omega - \epsilon_{\lambda})\} \quad (8)$$

$$= \frac{1}{2i\pi} \frac{\partial}{\partial\omega} \text{Tr}\{\ln[S(\omega)]\}. \quad (9)$$

Here ϵ and $\tilde{\epsilon}$ denote the energy levels of the original ($t \rightarrow -\infty$) and the emerging (relevant $t \approx 0$) system, respectively. The energy differences $\tilde{\epsilon}_{\lambda} - \epsilon_{\lambda}$ are, in principle, specified by the same formal collision theory arguments [134, 135] which underpin the expansion (3) but here pertain to the SP LS solutions [124]. The level shifts are only infinitesimal when considered per level but produce, as in all Friedel-phase-shift analysis [130], an integral effect which constitutes the full (noninteracting-particle) thermodynamic grand potential variation¹³ [147, 149],

$$\Delta\Omega_{\text{LS}} = \int_{-\infty}^{\mu_F} d\omega (\omega - \mu_F) \Delta\mathcal{D}(\omega) \quad (10)$$

$$= - \int_{-\infty}^{\mu_F} d\mu' \Delta\mathcal{N}(\mu'). \quad (11)$$

¹³References [147, 149, 150] are examples of equilibrium interaction studies that illustrate the formal equivalence in equilibrium of either moving to a canonical-ensemble evaluation or retaining the equilibrium Gibbs free energy term in a Harris scheme [151] adapted for the GCE thermodynamical DFT [52]. On the one hand, the stated form of the one-electron contribution, equation (4) in [147], can be viewed simply as an adjustment of the Fermi level; this canonical-ensemble approach is discussed and used in [152–154]. On the other hand, the expression for interaction energy (as expressed from one-electron contributions) also serves to explicitly include the Gibbs free energy term in an open-boundary thermodynamic evaluation. In that form it is consistent with a zero-temperature evaluation of Mermin's equilibrium thermodynamic DFT [52]. Either way, a careful handling of the implications of the Friedel sum rule plays a vital role in correctly describing charge conservation and the resulting interaction [2, 126, 147].

The key observation is that the formal result (7) applies for all values of μ' for noninteracting particles and that the S -matrix has an explicit on-shell character [138, 142, 149]. The formal scattering theory formulation (9) can be expanded in terms of the (on-shell) T -matrix. The procedure suggests a rapid convergence, for example, in a systematic calculation of the effective interaction between an adsorbate and a metal surface [149].

A textbook analysis [146] provides a simple example of the role of the phase-shift variation in thermodynamic calculations. The study of s-wave scatterers is relevant for a discussion of adsorbate-induced local-density-of-state changes in the metallic surface state (MSS) of Cu(111) [2, 126]. There one can have a simple (yet nonperturbative) T -matrix behavior [147, 155], $T_0^{\delta_F}(\omega) \propto \exp[i2\delta_0(\omega) - 1]$ (appendix A), which is completely characterized by the experimentally observed Fermi level phase-shift value [147], $\delta_F = \delta_0(\omega = \mu_F) \approx \pm\pi/2$. By assumption, the s-wave phase shift is the only eigenvalue of $\mathcal{S}(\omega)$, and inclusion of the s-wave scattering adsorbate causes a nonperturbative change in both the density of state and the equilibrium thermodynamic potential [146]

$$\Delta \mathcal{D}_{\text{MSS,1s}}^{\delta_F}(\omega) = \frac{2}{\pi} \frac{\partial}{\partial \omega} \delta_0(\omega), \quad (12)$$

$$\Delta \Omega_{\text{MSS,1s}}^{\delta_F} = -\frac{2}{\pi} \int_{-\infty}^{\mu_F} d\omega \delta_0(\omega). \quad (13)$$

The textbook result (13) is consistent with the formal thermodynamic result given by equations (7) and (11).

2.2. A finite-bias computational framework

For calculations of the thermodynamic behavior of nonequilibrium noninteracting tunneling it is natural to pursue a nonequilibrium Green function/scattering-state formulation which is effectively suggested in [148]. Under nonequilibrium conditions, we have left and right leads which are described by different chemical potentials $\mu_L > \mu_R$. The leads $P = L/R$ are formally of infinite volume \mathcal{V}_L and \mathcal{V}_R . Using the extensive nature of SP LS scattering solutions that arise from either lead one can define and evaluate the nonequilibrium noninteracting thermodynamic grand potential from a sum of partial terms

$$\Delta \Omega_{\text{LS}}(\mu_L, \mu_R) = \Delta \Omega_{\text{LS}}^L(\mu_L) + \Delta \Omega_{\text{LS}}^R(\mu_R), \quad (14)$$

$$\Delta \Omega_{\text{LS}}^{P=L/R}(\mu_P) = -\int_{-\infty}^{\mu_P} d\mu' \Delta \mathcal{N}_P(\mu'). \quad (15)$$

Here the value of $-\Delta \mathcal{N}_P/\mathcal{V}_P$ (for $P = L/R$) takes the role of a change in partial pressure given by the change in electron density (with, for example, the onset of tunneling). In a simple adaption of [148] it also follows that this partial pressure is given by well-defined components of the less-than Green function.

As further detailed in section 2.3, I consider a system which is initially disconnected ‘ d ’ but in which tunneling arises upon the adiabatic turn on. The connected system is generally identified by a superscript (0) as it is noninteracting. Relevant initial-system eigenstates $|\lambda_P\rangle$ of energy ϵ_{λ_P} are

those which belong to a lead, $P = L/R$. In the noninteracting tunneling systems, these initial eigenstates give rise to distinct [134, 135] SP LS solutions $|\tilde{\lambda}_P\rangle = |\psi_{\text{LS},\lambda_P}^{(0)}\rangle$ of energy $\tilde{\epsilon}_{\lambda_P}$. The resulting eigenstate set is (for noninteracting particles) orthonormal [135] and complete; I do not here explicitly consider effects of possible bound states [134]. The states $|\tilde{\lambda}_P\rangle$ are eigenstates of the connected system, and the initial and resulting electron distributions can conveniently be described by lead ‘ P ’ and state-specific contributions,

$$g_{<}^{(0)}(\tilde{\lambda}_P, \omega) = \delta(\omega - \tilde{\epsilon}_{\lambda_P}) f_{\mu=\mu_P}(\omega), \quad (16)$$

$$g_{<}^d(\lambda_P, \omega) = \delta(\omega - \epsilon_{\lambda_P}) f_{\mu=\mu_P}(\omega), \quad (17)$$

where, at a given chemical potential μ ,

$$f_{\mu}(\omega) = \frac{1}{1 + \exp[\beta(\omega - \mu)]} \quad (18)$$

denotes the Fermi–Dirac distribution function. An evaluation of the level shifts $\tilde{\epsilon}_{\lambda_P} - \epsilon_{\lambda_P}$ determines the partial pressures and GCE thermodynamics [148] via lead-projected density of state changes

$$\Delta \mathcal{D}_{P=L/R}(\omega) = 2 \sum_{\lambda_P} [\delta(\omega - \tilde{\epsilon}_{\lambda_P}) - \delta(\omega - \epsilon_{\lambda_P})], \quad (19)$$

and corresponding integrated density of state changes

$$\Delta \mathcal{N}_P(\mu') = \int_{-\infty}^{\mu'} \Delta \mathcal{D}_P(\omega) d\omega \quad (20)$$

$$= 2 \sum_{\lambda_P} \int \frac{d\omega}{2\pi} [g_{<}^{(0)}(\tilde{\lambda}_P, \omega) - g_{<}^d(\tilde{\lambda}_P, \omega)]. \quad (21)$$

Section 8.4 suggests use of the formal specification (21) to determine also the interacting nonequilibrium thermodynamic variation through the DFT SP formulation.

Figure 1 shows the schematics of the S -matrix eigenstate analysis, appendix B, that leads to an alternative formulation and interpretation of (15) based on scattering phase shifts [130, 144, 145]. The approach exploits the fact that for noninteracting particles, the S -matrix, and hence the Friedel sum rule (7), already contains a complete mapping of the mutually independent SP dynamics. I note that the S -matrix is specified by the T -matrix behavior, i.e., by the independent nature of the SP LS eigenstates [142, 149] and that there is no difference between the Green function framework (above) and the scattering phase formulation (below).

In essence the analysis uses the generalized Friedel sum rule formulation (7) to sort the SP contributions according to the lead from which the scattering states emerge. This is done simply by restricting the trace to initial states in either lead, appendix B. The key step is expressing the S -matrix eigenstates $|j\rangle$ of eigenvalue $\exp[2i\delta_j(\omega)]$ in original states ‘ $|\lambda_{P=L/R}\rangle$ ’ and obtaining a unitary matrix $\alpha = \langle j|\lambda_P\rangle$ for the representation change. For each initial state $|\lambda_P\rangle$ one can extract the independent SP dynamics from the noninteracting S -matrix, a step which identifies lead- and state-specific phase shifts

$$\delta_{\lambda_P}(\omega) \equiv \sum_j \delta_j(\omega) |\langle j|\lambda_P\rangle|^2 \quad (22)$$

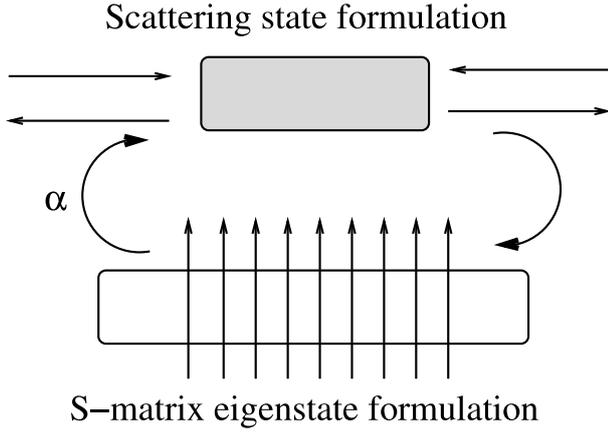


Figure 1. Schematics of the S -matrix decomposition analysis that is used here for a formal expression and interpretation of general thermodynamic grand potential changes. The essential step is identifying the unitary transformation (curved arrows) $\alpha = \langle j | \lambda_{L/R} \rangle$ which relates the mutually independent scattering of lead-specific initial states $|\lambda_{L/P}\rangle$ (upper panel) with the eigenstates $|j\rangle$ of the S -matrix (lower panel). The S -matrix decomposition provides a formal evaluation of the thermodynamic potential value in terms of effective (projected) phase shifts.

$$= \frac{1}{2i} \langle \lambda_P | \ln[S(\omega)] | \lambda_P \rangle. \quad (23)$$

The lead-and-state-specific contribution to the (tunneling-induced) change in density of state can thus be expressed in a familiar Friedel-type analysis [130]

$$\delta(\omega - \tilde{\epsilon}_{\lambda_P}) - \delta(\omega - \epsilon_{\lambda_P}) \leftrightarrow \frac{1}{2\pi} \frac{\partial}{\partial \omega} \delta_{\lambda_P}(\omega). \quad (24)$$

The S -matrix analysis (24) implies in turn an evaluation of (20) which simply involves restricting the trace in the Friedel sum rule (7) to initial-system eigenstates in either of the leads. Also, one may from (23) define corresponding frequency-dependent lead-specific phase shifts $\delta_{P=L/R}^{\text{eff}}(\omega)$ that satisfy

$$\delta_{P=L/R}^{\text{eff}}(\omega) \sum_{\lambda_P} \delta(\omega - \epsilon_{\lambda_P}) = \sum_{\lambda_P} \delta(\omega - \epsilon_{\lambda_P}) \delta_{\lambda_P}(\omega). \quad (25)$$

The effective phase shifts reflect the density of states in the leads. An alternative formal determination of lead-specific integrated density of state changes is then

$$\Delta \mathcal{N}_{P=L/R}(\mu_P) = \frac{2}{\pi} \delta_P^{\text{eff}}(\mu_P). \quad (26)$$

Similarly, the S -matrix eigenstate decomposition for non-interacting particles thus leads to a scattering phase-shift expression for the lead-specific contributions

$$\Delta \Omega_{LS}^{P=L/R}(\mu_P) = -\frac{2}{\pi} \int_{-\infty}^{\mu_P} d\omega \delta_P^{\text{eff}}(\omega) \quad (27)$$

to the nonequilibrium thermodynamic grand potential (14).

2.3. Role of the Gibbs free energy in surface interactions

The single-s-wave scatterer result (13) points to the central importance of Gibbs free energy changes. I

shall focus the discussion on the adsorption interaction effects that are observable in scanning-tunneling microscopy investigations [2, 126]. The importance is made explicit by noting that the equilibrium Gibbs free energy, here evaluated as

$$\begin{aligned} \mu_F \Delta \mathcal{N}_{\text{MSS},1s}^{\delta_F}(\mu_F) &= \mu_F \int_{-\infty}^{\mu_F} d\omega \Delta \mathcal{D}_{\text{MSS},1s}^{\delta_F}(\omega) \\ &= \mu_F \frac{2}{\pi} \delta_0(\mu_F), \end{aligned} \quad (28)$$

is specified by the Friedel sum rule (7). The scanning-tunneling microscopy observations [126] of Fermi level (s-wave) phase shifts $\delta_F \approx \pm\pi/2$ are a direct indication that the adsorbate causes strong changes in the Gibbs free energy.

The importance of Gibbs free energy variation in general open-infinite problems is further illustrated by calculations [4, 147, 152–155] of indirect electronic interaction arising between adsorbates on a noble metal surface and mediated by the MSS [2]. Previous presentations have summarized the GCE evaluation [52, 147, 149] of the resulting MSS-mediated interaction [2, 4, 126, 147, 155]. Here I provide a simple discussion of the underlying GCE thermodynamic behavior.

The analysis of the interaction problem involves (appendix A) a determination of additional scattering-induced changes in the integrated density of state (7). This calculation proceeds through the use of Lloyds' formula [156] and the result [147, 157] is given relative to the single-s-wave characterization, (28) and (13). From the determination of the integrated density of state changes (A.13) one directly extracts the noninteracting-particle result for both the internal and GCE Gibbs free energy variations

$$\Delta U_{\text{MSS},2s}^{\delta_F}(d; \mu_F) = \int_{-\infty}^{\mu_F} d\omega' \omega' \frac{\partial}{\partial \omega} \Delta \mathcal{N}_{\text{MSS},2s}^{\delta_F}(d; \omega'), \quad (29)$$

$$\Delta Y_{\text{MSS},2s}^{\delta_F}(d; \mu_F) = \mu_F \Delta \mathcal{N}_{\text{MSS},2s}^{\delta_F}(d; \mu_F). \quad (30)$$

Use of formal Fourier transform analysis [158] establishes the (leading) asymptotic behavior of both of these terms as oscillatory but with a $1/d$ decay. The net (zero-temperature) interaction is given by the variation in thermodynamic grand potential

$$\Delta \Omega_{\text{MSS},2s}^{\delta_F}(d; \mu_F) \equiv \Delta U_{\text{MSS},2s}^{\delta_F}(d; \mu_F) - \Delta Y_{\text{MSS},2s}^{\delta_F}(d; \mu_F) \quad (31)$$

$$\sim -\epsilon_F \left(\frac{2 \sin(\delta_F)}{\pi} \right)^2 \frac{\sin(2q_F d + 2\delta_F)}{(q_F d)^2}, \quad (32)$$

where ϵ_F denotes the difference between μ_F and the bottom of the MSS band. The last expression (32) states the asymptotic behavior.

The thermodynamic grand potential interaction results [4, 147], the asymptotic oscillatory $1/d^2$ decay, and the phase in (32) correspond well with experimental observations [2, 126] for adatoms and admolecules on Cu(111). However, I stress that this correct interaction behavior only arises upon a cancellation of terms with a much larger $1/d$ leading-order behavior. This observation illustrates the essential role that charging, i.e., the Gibbs free energy variation and adherence to the Friedel sum rule, plays in understanding the GCE systems.

2.4. Role of the Gibbs free energy in nonequilibrium tunneling

In nonequilibrium tunneling the Gibbs free energy is no less important since it describes charge adjustments and thus thermodynamic changes arising with the onset of tunneling. It thus affects the nature of nonequilibrium thermodynamic forces that guide strictly adiabatic transformations, i.e., forces that are applicable (and needed) in the limit when the masses of the ions can be seen as infinitely greater than the mass of the electrons.

The top panel of figure 2 shows a schematic of a type of resonant tunneling problem in which it is relevant to study both (nonadiabatic) electromigration [87] and nonequilibrium adiabatic relaxations from an exact thermodynamic analysis. I stress that there is only a limited zone of overlap in the nature and applicability of the here-derived adiabatic thermodynamic forces and the electrostatic forces investigated in the standard electromigration literature, for example, summarized in [87]. In general, the electromigration literature [87] splits the nonequilibrium forces into a wind force contribution \mathbf{F}_w , defined by an electron–nucleus momentum transfer, and a direct force \mathbf{F}_d . The wind force is proportional to the current density vector $\mathbf{J}(\mathbf{r})$, but is never relevant for a discussion of strictly adiabatic transformations (i.e., when one assumes an infinite ratio of the nucleus mass to the electron mass). The direct force \mathbf{F}_d is generally assumed to be electrostatic in nature, and typically assumed to be proportional to $\mathbf{J}(\mathbf{r})$, although there are also observations that the electrostatic nature can be more complex [103]. There are arguments that an electrostatic nature of \mathbf{F}_d is relevant in linear response [87, 98]. However, there is no rigorous demonstration for a general equivalence of electrostatic and thermodynamic forces, section 6.3.

An example of the nonequilibrium Gibbs free energy effect, also shown in figure 2, is motivated to help illustrate the differences between thermodynamic forces and nonconservative electrostatic forces that are proportional to $\mathbf{J}(\mathbf{r})$. The example shows that there is no formal conflict with the Sorbello gedanken experiment (explained, for example, in [103, 106]) because that analysis is not complete in the discussion of strictly adiabatic thermodynamic changes. The Sorbello gedanken experiment represents an argument that the nonequilibrium forces should be nonconservative if they are proportional to the current density. A force relation (a proportionality) to the current density vector is seen as the fundamental reason that the electrostatic forces can sometime acquire a nonconservative nature [103, 106]. However, the assumption that $\mathbf{F} \propto \mathbf{J}(\mathbf{r})$ cannot generally be relevant—and I find that the Sorbello gedanken experiment is not conclusive—for an analysis of adiabatic thermodynamic forces. This follows because such forces omit a full treatment of the nonequilibrium Gibbs free energy variation.

The middle and bottom panels of figure 2 summarize an analysis of the thermodynamic changes (defined by level-occupation changes) that must arise in simple resonant tunneling systems when adiabatically moving the resonant level from a position ‘AW’ to another position ‘BW’

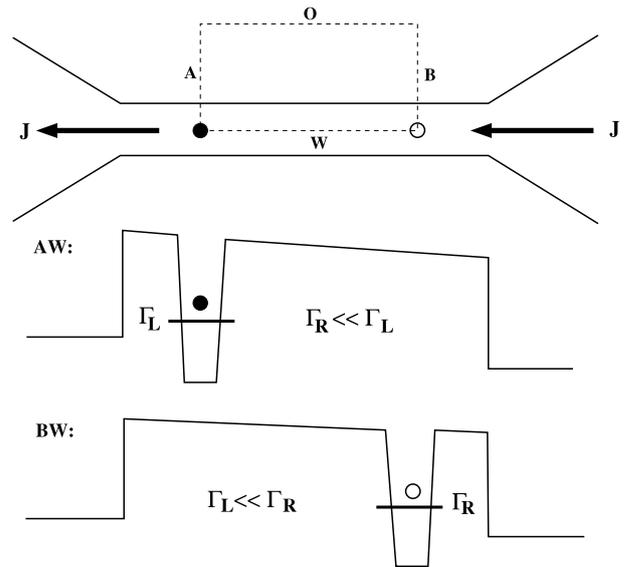


Figure 2. Schematics of possible (adiabatic) translations (inside the current-carrying wire, W, or outside, along path legs A, O, B) of the resonant level position in a lower-dimensional resonant tunneling system and identification of a nonequilibrium Gibbs free energy effect (associated with resonant level charging) that requires a thermodynamic force analysis. The charging or discharging is independent of whether the resonant level is moved inside or outside of the wire. The nonequilibrium Gibbs free energy (as well as the total nonequilibrium thermodynamic grand potential) variation cannot be captured by forces which are proportional to the current density vector \mathbf{J} (arrow in top panel) but will generally arise (via changes in the scattering phase shifts) also when the resonant level (or defect or ion) is moved perpendicularly to \mathbf{J} , along path legs A and B.

(positions which are intersections of the set of path legs shown in the top panel). These are changes that arise when the resonant level goes from a charged state (filled circle) to a discharged state (empty circle) and creates different regimes of tunneling [42, 46]. The nonequilibrium interactions in such systems have for example been explored in [37, 41] and the changes in occupation cause differences in the nature and strength of the many-body interactions [42, 129]. A strictly adiabatic transformation along different paths must still produce the same (uniquely defined) final steady-state solution and, in particular, identical changes in the thermodynamic grand potential and Gibbs free energy values, section 6.4.

I stress that the above-described adiabatic change in Gibbs free energy arises exclusively in the presence of a finite applied bias. I observe that the nonequilibrium Gibbs free energy change will arise (from phase-shift changes) also when moving the resonant level position perpendicularly to the current flow (along path legs A and B). Figure 2 thus identifies a nonequilibrium Gibbs free energy and thermodynamic grand potential change which will not (generally) turn up in a path integral of the electromigration-type of forces (that satisfy $\mathbf{F} \propto \mathbf{J}(\mathbf{r})$).

I conclude that an analysis of exact thermodynamic forces for strictly adiabatic transformations may sometimes

be necessary to supplement the standard electromigration analysis [87].

3. Partition scheme and Hamiltonian

The partition scheme of Caroli *et al* [32] allows a description of tunneling which is first principle and predictive (i.e., parameter-free, atomistic). This is true when the Caroli partition scheme is extended from the original tight-binding framework to the continuum formulation [33, 64]. The emphasis on an atomistic approach (i.e., with the description of the electron dynamics having a parametric dependence on the nuclei positions) is important because we desire a thermodynamic theory specific to the material's nature. Avoiding an empirical modeling (set, e.g., by tight-binding parameters) implies that the electron behavior is completely specified by the positions of the nuclei and by whatever external field one chooses to apply. Subject to a suitable nonequilibrium implementation of the Born–Oppenheimer approximation, one can therefore relax the atomic structure and morphology to provide a parameter-free and fully predictive thermodynamic description of interacting nonequilibrium tunneling starting from an electron Hamiltonian.

3.1. Initially disconnected equilibria system

Using atomic units throughout, the total kinetic energy can be expressed as a formal second-quantization operator

$$K = \sum_s \int d\mathbf{r}' \int d\mathbf{r} \hat{\psi}_s^\dagger(\mathbf{r}') \frac{1}{2} \langle \mathbf{r}' | \hat{k}^2 | \mathbf{r} \rangle \hat{\psi}_s(\mathbf{r}), \quad (33)$$

$$\langle \mathbf{r}' | \hat{k}^2 | \mathbf{r} \rangle = - \int d\mathbf{r}_1 \frac{\partial}{\partial \mathbf{r}'} \delta(\mathbf{r}' - \mathbf{r}_1) \frac{\partial}{\partial \mathbf{r}_1} \delta(\mathbf{r}_1 - \mathbf{r}). \quad (34)$$

This formulation reduces to the traditional second-quantization form

$$K = \sum_s \int d\mathbf{r} \hat{\psi}_s^\dagger(\mathbf{r}) \left(-\frac{1}{2} \nabla^2\right) \hat{\psi}_s(\mathbf{r}), \quad (35)$$

with a handling of boundary conditions.

The Feuchtwang/Caroli partition scheme [32, 33, 40] for nonequilibrium Green function and/or wavefunction studies of tunneling assumes that the system is disconnected at $t \rightarrow -\infty$, split into three sections, and has a kinetic energy described by $K - \delta K$. The tunneling term δK is defined below but is adiabatically turned on,

$$K(t) = (K - \delta K) + \delta K(t), \quad (36)$$

$$\delta K(t) \sim \delta K \exp(\eta t) \quad (37)$$

so that the full kinetic energy (35) emerges at $t = 0$. The $t \rightarrow 0$ splitting into disconnected sections allows the thermodynamics to be unambiguously defined in each of the components, a left lead ‘L’ ($z < z_L$), a center region ‘C’ ($z_L < z < z_R$), and a right lead ‘R’. This Caroli partition scheme has, for example, been used to derive a generalization of the Landauer–Büttiker-type current formula to interacting tunneling [37, 38]. The total kinetic energy K of the system

is written as a sum, $K \equiv K_L + K_R + K_C + \delta K$, where $K_{L,R,C}$ have supports which are confined to the respective, separate components.

The continuum (and thus atomistic) Caroli partition scheme [33, 40, 64] assumes that each of the disconnected subsections $H_d = \sum_{J=L,C,R} H_J$ is in equilibrium at different chemical potentials $\mu_{L/C/R}$ and that the three spatial regions of H_d together can represent the full spatial variation of any given potential $v(\mathbf{r}, t)$. At $t \rightarrow -\infty$, the system is assumed to be described by the static external potential $v_d(\mathbf{r})$ and corresponding operator

$$V_d = \int d\mathbf{r} v_d(\mathbf{r}) \hat{n}(\mathbf{r}), \quad (38)$$

where $\hat{n}(\mathbf{r}) \equiv \sum_s \psi_s^\dagger(\mathbf{r}) \hat{\psi}_s(\mathbf{r})$ denotes the electron-density operator.

The initial system in the continuum (and hence atomistic) Caroli scheme is simply

$$H_d = \sum_{P=L/R/C} K_P + V_d. \quad (39)$$

I use $\{c_{\lambda,P=L/R/C}^\dagger\}$ to denote the set of operators which creates an electron in an H_d SP eigenstate (of energy $\epsilon_{\lambda,i}$) with basis in the left, right, or center region, respectively. The quadratic Hamiltonian (39) can be expressed as

$$H_d = \sum_{J=L/R/C} \sum_{\lambda} \epsilon_{\lambda,J} c_{\lambda,J}^\dagger c_{\lambda,J}. \quad (40)$$

In a second-quantization formulation, the tunneling term can then be expressed as

$$\begin{aligned} \delta K &= \sum_s \int d\mathbf{r} \hat{\psi}_s^\dagger(\mathbf{r}) \left[-\frac{1}{2} \nabla^2 + v_d(\mathbf{r})\right] \hat{\psi}_s(\mathbf{r}) \\ &\quad - \sum_{J=L/R/C} \sum_{\lambda} \epsilon_{\lambda,J} c_{\lambda,J}^\dagger c_{\lambda,J}. \end{aligned} \quad (41)$$

This is a traditional starting point in nonequilibrium Green function calculations.

Figure 3 suggests that this Caroli framework can be interpreted as representing a system which at $t \rightarrow -\infty$ (and around the divisions $z_{L/R}$) has voids of high fictitious barriers of width $l_{L/R} \rightarrow \infty$. At a finite time, the width $l_{L/R}(t)$ of the fictitious barriers decreases (and eventually vanishes at $t = 0$) so as to produce the actual form of the adiabatic turn on of the tunneling term $\delta K(t) \sim \delta K \exp(\eta t)$. I stress that the precise formulation of δK or interpretations is irrelevant for the formal results presented here and for all parts of the previous LS collision DFT analysis¹⁴ [64].

The precise formulation and expression for δK (including the choice of $z_{L/R}$) are also of no consequence for practical

¹⁴The explicit form given for the tunneling term δK in [64] is not correct. However, that fact is completely irrelevant for the formal exploration of the tunneling based on the Caroli partition, $K = (K - \delta K) + \delta K$ (an equation which formal scattering theory solves to all orders in δK). For example, in the uniqueness of density proof presented in the appendix of [64], the specific form for δK is completely void of consequence since the difference between two relevant Hamiltonians will always exclusively depend on a possible difference in the external potentials.

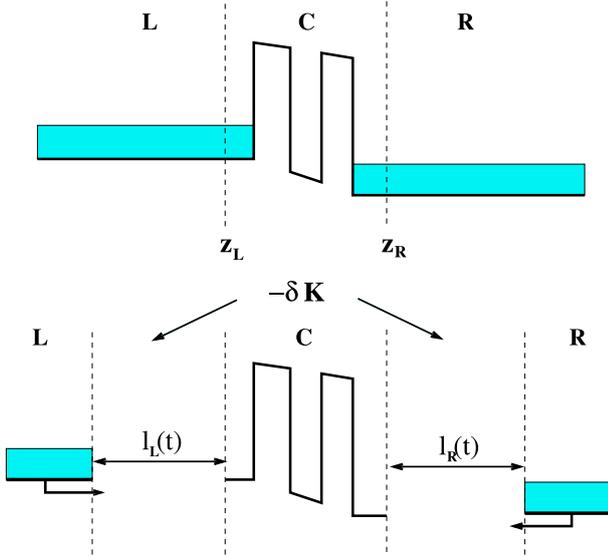


Figure 3. Schematic of a possible interpretation of the continuum Caroli partition scheme. In the interpretation one assumes that the three sections (a left ‘L’ and right ‘R’ lead, and a center tunneling region ‘C’) are split at z_L and z_R (shown in the top panel) and well separated (bottom panel) at $t \rightarrow -\infty$, thus ensuring a well-characterized equilibrium thermodynamics starting point for the quantum-kinetic account. The starting kinetic energy differs by δK from that of the connected system that characterizes the system at $t = 0$ (top panel). The kinetic-energy difference δK is adiabatically turned on together with changes in the single-particle potential δV and a general electron–electron interaction term W . I stress that the actual partition scheme (formulated in the text) is independent of this schematic interpretation; it is simply a well defined and standard second-quantization starting point for computing properties of interacting nonequilibrium tunneling [37, 38, 64].

nonequilibrium thermodynamic calculations. This is because I here demonstrate that the relevant thermodynamics can be expressed through the phase shifts of the SP LS solutions [118, 124], a quantity for which there exist readily available efficient solvers. In fact, I show that the SP standard DBT codes [118–122] (for frozen-nuclei problems) already approximate the exact SP LS solutions and, moreover, can be adapted also for systematic improvements (given refinement of the nonequilibrium density functional description).

A simple Gibbs weighting operator \hat{X}_d and associated unnormalized density matrix

$$\hat{\rho}_d \equiv \exp[-\beta \hat{X}_d] \quad (42)$$

characterize the disconnected ($t \rightarrow -\infty$) system at inverse temperature β . The initial density matrix is a direct product of L/C/R equilibrium density matrices and the initial Gibbs weighting can therefore directly be expressed as a difference

$$\hat{X}_d \equiv H_d - \hat{Y}_d \quad (43)$$

between H_d and an operator for the $t \rightarrow -\infty$ Gibbs free energy,

$$\hat{Y}_d \equiv \sum_{J=L/R/C} \mu_J \hat{c}_{\lambda,J}^\dagger \hat{c}_{\lambda,J}. \quad (44)$$

It is possible (and likely helpful for nonequilibrium thermodynamic calculations) to define the initial disconnected equilibria system H_d as composed of isolated ground-state DFT systems. One may, for example, adapt the embedding formulation [159] from the original application for surfaces and to the present case of (infinitely extended) barriers around $z_{L/R}$. In such an embedding approach it may furthermore be convenient to assume that the form of $v_d(\mathbf{r})$ for $\mathbf{r} \rightarrow \pm\infty$ reduces to that of a jellium model, i.e., describing a uniform background potential $\phi_{L/R}$ for $z \rightarrow \pm\infty$. The values of ϕ_L and ϕ_R must be chosen to ensure charge neutrality of the initial, disconnected Hamiltonian at $t \rightarrow -\infty$ (and at $z \rightarrow \pm\infty$ in general).

The continuum Caroli partition scheme ensures that we have initially a disconnected equilibria configuration and therefore a well-defined thermodynamics starting point. The disconnected equilibria ($t \rightarrow -\infty$) density matrix

$$\frac{\hat{\rho}_d}{\text{Tr}\{\hat{\rho}_d\}} = \frac{\exp[-\beta(H_d - \hat{Y}_d)]}{\text{Tr}\{\exp[-\beta(H_d - \hat{Y}_d)]\}} \quad (45)$$

is independent of the value of the applied bias $\phi_{\text{bias}} \equiv \phi_L - \phi_R = \mu_L - \mu_R$. I stress that the interacting tunneling system will evolve to gain the correct density distribution and that the relation $\phi_L - \phi_R = \mu_L - \mu_R$ is not used at relevant times $t \approx 0$. The initial density matrix depends exclusively on the initial electron concentration in the leads and the pair of values for lead chemical potentials, and, when relevant, on the initial occupation (formally described by the chemical potential μ_C) of the central island ‘C’ [64].

3.2. The interacting tunneling system

The continuum Caroli partition scheme assumes an adiabatic turning on of the fixed tunneling term δK of a given many-body interaction W (for example, the full electron–electron interaction) and of a static electron scattering potential $v_{\text{sc}}(\mathbf{r})$ which includes the effects of the applied bias and of the set of atomic potentials. The scheme can also allow for an additional time-dependent potential $\phi_g(\mathbf{r}, t > t_g)$, then describing a gate operation starting at some finite time t_g . The total (time-dependent) collision potential is

$$v_{\text{col}}(\mathbf{r}, t) = v_{\text{sc}}(\mathbf{r}) + \phi_g(\mathbf{r}, t). \quad (46)$$

This single-particle potential defines a quadratic contribution

$$V_{\text{col}}(t) = \int d\mathbf{r} v_{\text{col}}(\mathbf{r}, t) \hat{n}(\mathbf{r}) \quad (47)$$

to the Hamiltonian.

In several cases in the presentation of a thermodynamic theory for tunneling, the focus will be on the steady-state regime. Here the collision term simply describes the effect of the time-independent scattering potential

$$V_{\text{col}}(t) \longrightarrow V_{\text{sc}} = \int d\mathbf{r} v_{\text{sc}}(\mathbf{r}) \hat{n}(\mathbf{r}). \quad (48)$$

For a continuum description (which allows atomistic calculations) of electron dynamics in nonequilibrium interacting tunneling, I investigate the full quantum-kinetics of the

electrons in the connected (time-dependent and interacting) Hamiltonian

$$H(t) = H_d + a_\eta(t) H_{1,\text{col}}(t), \quad (49)$$

$$H_{1,\text{col}}(t) = \{\delta K + W + V_{\text{col}}(t) - V_d\}. \quad (50)$$

The adiabatic turn on is described by a factor $a_\eta(t)$ which for all practical purposes¹⁵ can be taken as $\exp(\eta t)$, $\eta \rightarrow 0$; the original LS analysis [123] of the many-body collision problems used $\exp(-\eta|t|)$, $\eta = 0^+$.

Furthermore, to aid the discussion of an exact, effective SP formulation (for efficient calculations of the nonequilibrium density, thermodynamic grand potential and forces) in steady state, I also introduce the quadratic Hamiltonian

$$H_V^{(0)} \equiv H_d + H_{1,V}^{(0)}, \quad (51)$$

$$H_{1,V}^{(0)} \equiv -V_d + \delta K + V, \quad (52)$$

where the potential term V is described by a time-independent scattering potential, $V = V_{\text{sc}}$.

3.3. Relation to the quantum-kinetics account

Both the original Caroli scheme and the presently used continuum Caroli partition scheme [33, 64] define a many-body collision problem [123] for nonequilibrium tunneling. Traditional many-body collision problems involve an approach of initially free particles to a central interacting collision region; this approach can conveniently be expressed by an adiabatic turn on, for example, as used in the formal LS formulation [123], and in subsequent analysis by, for example, Dyson [132], Pirenne [133], Gellmann and Goldberger [134] and DeWitt [135].

Reference [136] provides an excellent introduction and discussion of the application of formal collision theory to condensed matter theory problems. The trick of a soft turn on of the perturbations was soon applied also for (infinite) condensed matter problems to drive the system from a well-defined initial configuration to the physically relevant case of an interacting many-body system. The adiabatic turn on (and hence the inherent collision nature) is essential for the quantum-kinetics account of nonequilibrium dynamics [15] as well as specific Green function calculations of interacting tunneling as it provides such calculations with a robust starting point.

The steady-state Gibbs free energy operator coincides with the operator (originally termed ‘ \hat{Y} ’) that the steady-state ReNQSM uses to describe electron redistribution in the nonequilibrium density matrix

$$\hat{\rho}_{\text{LS}} \equiv \exp[-\beta(H - \hat{Y}_{\text{LS}})]. \quad (53)$$

¹⁵It is possible to link the LS collision DFT [64] with the present nonequilibrium thermodynamic account because one can make compatible choices in the details of adiabatic turn on and thus satisfy even stringent mathematical conditions, appendix D.

This redistribution operator can under general conditions be interpreted as [21, 22, 25]

$$\hat{Y}_{\text{LS}} = \sum_{\lambda,J=L/R/C} \mu_J \hat{\psi}_{\text{LS},\lambda,J}^\dagger \hat{\psi}_{\text{LS},\lambda,J}, \quad (54)$$

in terms of a family of operators $\{\hat{\psi}_{\text{LS},\lambda,J}^\dagger\}$ for many-body LS single-quasi-particle excitations of energy $\epsilon_{\lambda,P=L/R/C}$. For most transport problems, when bound states are not relevant, one can ignore the evolution which originates from the smaller number of states in the center regime. For simplicity in notation and discussion I will therefore restrict the summation for the connected system (and in (54)) simply to the scattering contributions originating from the leads, $P = L, R$.

In any case, the operators (54) express the adiabatic evolution (described by a many-body Liouville operator $\mathcal{L}_H \hat{A} \equiv [H, \hat{A}]$) of the initial (independent) states subject to full many-body interaction [21, 22],

$$\hat{\psi}_{\text{LS},\lambda,P}^\dagger = \frac{i\eta}{\epsilon_{\lambda,P} + \mathcal{L}_H + i\eta} \hat{c}_{\lambda,P}^\dagger. \quad (55)$$

This operator-based ReNQSM analysis can be generalized [23–27, 131, 157] and it is possible to express not only the general Gibbs free energy operator $\hat{Y}_{\text{col}}(t)$ but also the variational LS expression for the many-body T -matrix [64] in terms of single-quasi-particle excitations.

4. Nonequilibrium quantum statistical mechanics

The formal structure of the exact nonequilibrium thermodynamic theory is obtained in the spirit of Mermin’s 1965 formulation of equilibrium thermodynamics [52]. In the absence of any applied bias one regains the GCE system for which Mermin succeeded in formulating an equilibrium thermodynamic DFT.

4.1. Collision nature of transport

The general strategy for studying many-body collision problems is to formally solve for projections of the full time-evolution operator

$$i \frac{\partial \mathcal{U}(t, -\infty)}{\partial t} = H(t) \mathcal{U}(t, -\infty). \quad (56)$$

This operator describes, for example, the evolution of a many-body collision state

$$|\Psi_\xi(t)\rangle = \mathcal{U}(t, -\infty) |\Phi_\xi\rangle \quad (57)$$

originating and evolving from an initial state $|\Phi_\xi\rangle$. I shall assume that such initial states are simultaneous eigenstates of the disconnected-system operators H_d and \hat{Y}_d (of eigenvalues E_ξ and Y_ξ , respectively) and I expand the unnormalized, initial density matrix

$$\hat{\rho}_d \equiv \sum_{\xi} |\Phi_\xi\rangle \exp[-\beta(E_\xi - Y_\xi)] \langle \Psi_\xi|. \quad (58)$$

For a steady-state collision problem one can explicitly construct a nonequilibrium density matrix which incorporates the full complexity of the many-body LS solution [123] (3). The adiabatic turn on, including scattering and interactions, causes energy shifts Δ_ξ which are consistently handled within the general LS solution by simultaneously adjusting [133–135]

$$\delta V \rightarrow \delta V - \Delta_\xi |\Phi_\xi\rangle\langle\Phi_\xi|, \quad (59)$$

$$E_\xi \rightarrow E_\xi + \Delta_\xi. \quad (60)$$

The resulting LS solution

$$|\Psi_\xi^{(+)}\rangle = \frac{i\eta}{E_\xi - H + i\eta} |\Phi_\xi\rangle \quad (61)$$

constitutes an explicit construction of an interacting eigenstate of energy $E_\xi + \Delta_\xi$ for steady-state problems. The energy shifts [133] Δ_ξ are themselves determined by the state evolution [134–136]. In condensed matter problems such shifts are essential and permit applications also to problems where the perturbation includes a periodic potential (and the dynamics must reflect the band structure that arises) [134]. The inclusion of the integrated effects of (infinitesimal) energy shifts provides a consistent GCE determination of the indirect electronic interactions of adsorbates on surfaces [147].

Steady-state solutions arise in the collision problems when the collision potential reduces to the time-independent form (48) and when the system dynamics is completely specified by $H(t=0)$. The many-body LS solution (61) constitutes a projection of the time-evolution operator $\mathcal{U}(t, -\infty)$, since it satisfies

$$\exp(-i(E_\xi + \Delta_\xi)t) |\Psi_\xi^{(+)}\rangle = \mathcal{U}(t, -\infty) |\Phi_\xi\rangle \quad (62)$$

in the limit of an infinitely slow adiabatic turn on, $\eta \rightarrow 0^+$. Combining equations (58) and (62) yields an (unnormalized) steady-state nonequilibrium collision density matrix (3).

The explicit construction (3) of the steady-state nonequilibrium density matrix $\hat{\rho}_{LS}$ provides a direct link of the nonequilibrium thermodynamic theory (and of ReNQSM) to formal many-body LS solutions [123]. Closely related links are expressed in the seminal steady-state ReNQSM papers [21, 22] and in several recent extensions and applications that study steady-state interacting tunneling transport [23–28].

4.2. Collision picture of interacting tunneling

Standard QKA methods, including nonequilibrium Green function techniques, permit calculations of operator expectation values under nonequilibrium conditions and must therefore provide a consistent treatment of the collision nature (57). The tested versatility of the many-body LS equation for steady-state problems motivates an effort to keep a corresponding collision picture for solving general (time-dependent or steady-state) interacting tunneling through a nonequilibrium collision density matrix $\hat{\rho}_{col}(t)$.

Traditionally, the formal starting point for calculating the expectation value of an operator $\hat{O}(t)$ in a nonequilibrium system is [15]

$$\langle\hat{O}\rangle_{col}(t) \equiv \frac{\text{Tr}\{\hat{\rho}_d \hat{O}_{\mathcal{H}}(t)\}}{\text{Tr}\{\hat{\rho}_d\}}. \quad (63)$$

The subscript ‘col’ emphasizes that a Caroli collision picture underpins the definition. The evaluation (63) rests on the Heisenberg picture which represents a canonical transformation of operators,

$$\hat{O}(t) \longrightarrow \hat{O}_{\mathcal{H}}(t) \equiv \mathcal{U}^\dagger(t, -\infty) \hat{O}(t) \mathcal{U}(t, -\infty). \quad (64)$$

The Heisenberg picture has advantages for time-independent problems (as it leaves the many-body eigenstates fixed), but it is not a natural description in the presence of the adiabatic turn on used in the collision problems. Nevertheless, the original $t \rightarrow -\infty$ system (H_d) has a well-defined separated-equilibrium thermodynamics $\hat{\rho}_d$. The formulation (63) still serves to uniquely define the expectation value because the QKAs emphasize accurate (conserving) descriptions of the time evaluation $\mathcal{U}(t, \infty)$.

For development of a nonequilibrium thermodynamic theory it is more advantageous to make the collision nature (57) explicit in the operators for thermodynamic quantities. I work below with a collision picture defined by operator transformations

$$\hat{A}(t) \longrightarrow \hat{A}_{col}(t) \equiv \mathcal{U}(t, -\infty) \hat{A}(t) \mathcal{U}^\dagger(t, -\infty), \quad (65)$$

where $\hat{A}(t)$ denotes a time-dependent operator in the Schrödinger picture. This is done simply because it offers a simpler formulation and interpretation; the here-presented description is formally exact. This approach is suggested by the formal steady-state LS solution [123] and it is here used for a general time-dependent tunneling case. In such a collision picture we obtain an explicit construction of the exact nonequilibrium collision density matrix

$$\begin{aligned} \hat{\rho}_{col}(t) &\equiv \mathcal{U}(t, -\infty) \hat{\rho}_d \mathcal{U}^\dagger(t, -\infty) \\ &= \sum_\xi |\Psi_\xi(t)\rangle \exp[-\beta(E_\xi - Y_\xi)] \langle\Psi_\xi(t)|. \end{aligned} \quad (66)$$

The time evaluation of the density matrix is

$$i \frac{d\hat{\rho}_{col}}{dt} = [H(t), \hat{\rho}_{col}(t)]. \quad (67)$$

The formal time evolutions of other operators are also simpler than in the Heisenberg picture because of the opposite ordering of time-evolution operators in (66). In using the collision picture for thermodynamic operators (65) care is taken to verify that the resulting formulation remains exact and fully equivalent with the traditional formulations of the QKA [15]. For the collision density matrix (66) the formal equivalence

$$\langle\hat{O}\rangle_{col}(t) \equiv \frac{\text{Tr}\{\hat{\rho}_d \hat{O}_{\mathcal{H}}(t)\}}{\text{Tr}\{\hat{\rho}_d\}} = \frac{\text{Tr}\{\hat{\rho}_{col}(t) \hat{O}(t)\}}{\text{Tr}\{\hat{\rho}_{col}(t)\}} \quad (68)$$

follows simply from a cyclic permutation of operators.

4.3. Thermodynamical description of nonequilibrium tunneling

The collision density matrix (66) can be expressed in terms of an evolving Gibbs weighting factor $\hat{X}_{\text{col}}(t)$. I start from the disconnected-equilibrium Gibbs weighting

$$\hat{X}_{\text{col}}(t \rightarrow -\infty) = \hat{X}_{\text{d}} \equiv H_{\text{d}} - \hat{Y}_{\text{d}}, \quad (69)$$

and express the evolution

$$\hat{X}_{\text{col}} = \mathcal{U}(t, -\infty) \hat{X}_{\text{d}} \mathcal{U}^\dagger(t, -\infty), \quad (70)$$

$$\hat{\rho}_{\text{col}}(t) = \exp[-\beta \hat{X}_{\text{col}}(t)], \quad (71)$$

thus identifying (70) as the emerging Gibbs weighting.

The introduction of a nonequilibrium Gibbs weighting factor motivates, in turn, a definition of the thermodynamic grand potential

$$\begin{aligned} \Omega_{\text{col}}(t) &\equiv -\frac{1}{\beta} \ln \text{Tr}\{\hat{\rho}_{\text{col}}(t)\} \\ &= -\frac{1}{\beta} \ln \text{Tr}\{\exp[-\beta \hat{X}_{\text{col}}(t)]\}. \end{aligned} \quad (72)$$

The exact ReNQSM [21, 22, 24] shows that $H - Y_{\text{LS}}$ serves as a Gibbs weighting factor in the steady-state problem. For the general tunneling problem I define

$$\hat{Y}_{\text{col}}(t) \equiv H(t) - \hat{X}_{\text{col}}(t), \quad (73)$$

corresponding to a reformulation the normalized collision density matrix

$$\frac{\hat{\rho}_{\text{col}}(t)}{\text{Tr}\{\hat{\rho}_{\text{col}}(t)\}} = \exp[\beta[\Omega_{\text{col}}(t) - H(t) + \hat{Y}_{\text{col}}(t)]]. \quad (74)$$

A formal evaluation of the entropy $S_{\text{col}}(t)$ in the exact collision density matrix can therefore be expressed as [11]

$$\begin{aligned} S_{\text{col}}(t) &\equiv -\langle \ln(\hat{\rho}_{\text{col}}) \rangle_{\text{col}} + \langle \ln(\text{Tr}\{\hat{\rho}_{\text{col}}\}) \rangle_{\text{col}} \\ &= -\beta \Omega_{\text{col}}(t) + \beta \langle H(t) \rangle_{\text{col}} - \beta \langle \hat{Y}_{\text{col}}(t) \rangle_{\text{col}}. \end{aligned} \quad (75)$$

I consequently make the natural identification of $\hat{Y}_{\text{col}}(t)$ as the operator for the nonequilibrium Gibbs free energy and I stress that the operator can be seen as emerging, with a time evolution given by the LS collision picture (65). This interpretation is consistent with the boundary condition,

$$\hat{Y}_{\text{col}}(t \rightarrow -\infty) = \hat{Y}_{\text{d}} = \sum_{\lambda, J=L/R/C} \mu_J \hat{c}_{\lambda, J}^\dagger \hat{c}_{\lambda, J}, \quad (76)$$

which obviously provides an explicit formulation of the Gibbs free energy in the original, disconnected equilibria system. I note that, irrespective of the interpretation, the operator $\hat{Y}_{\text{col}}(t)$ is uniquely specified by the collision nature of the Gibbs weighting operator $\hat{X}_{\text{col}}(t)$ or, equivalently, of the exact collision density matrix (71).

4.4. Nonequilibrium Gibbs free energy

An evaluation of the exact collision density matrix (71) requires an explicit determination of the operator for the nonequilibrium Gibbs free energy, $\hat{Y}_{\text{col}}(t)$. This was (with

the interpretation stated above) a central achievement of the exact steady-state ReNQSM, proceeding through an explicit construction \hat{Y}_{LS} order-by-order in the formal perturbation term [21]. Here I start instead with the collision nature of the problem, to obtain a generalization to general tunneling and to clarify the explicit connection to a full nonequilibrium thermodynamic theory.

By the emerging nature of the Gibbs free energy operator (73), we can directly extract the formal time evolution

$$i \frac{d\hat{Y}_{\text{col}}(t)}{dt} = [H(t), \hat{Y}_{\text{col}}(t)] + i \frac{dH(t)}{dt}, \quad (77)$$

a differential equation which, of course, must be solved subject to the (collision) boundary condition $Y_{\text{col}}(t \rightarrow -\infty) = \hat{Y}_{\text{d}}$. For the set of operators $\{\hat{c}_{\lambda P=L/R/C}^\dagger\}$ which (at $t \rightarrow -\infty$) describes creation of single-particle H_{d} eigenstates (of single-particle energies $\epsilon_{\lambda P=L/R/C}$.) we can formally establish the time evolution in the collision picture

$$\hat{c}_{\lambda P}^\dagger \longrightarrow \hat{\psi}_{\lambda P}^\dagger(t) = \mathcal{U}(t, -\infty) \hat{c}_{\lambda P}^\dagger \mathcal{U}^\dagger(t, -\infty). \quad (78)$$

In turn, the formal solution (78) provides an explicit determination of the operator for the emerging Gibbs free energy operator

$$\hat{Y}_{\text{col}}(t) = \sum_{\lambda P=L/R} \mu_P \hat{\psi}_{\lambda P}^\dagger(t) \hat{\psi}_{\lambda P}(t). \quad (79)$$

The exact nonequilibrium Gibbs free energy value is calculated from (79) and from the uniquely specified nonequilibrium solution density matrix,

$$Y_{\text{col}}(t) = \frac{\text{Tr}\{\hat{Y}_{\text{col}}(t) \hat{\rho}_{\text{col}}(t)\}}{\text{Tr}\{\hat{\rho}_{\text{col}}(t)\}}. \quad (80)$$

For problems with a time-independent scattering potential $v_{\text{sc}}(\mathbf{r})$, and when an actual steady-state transport results, the emerging Gibbs free energy \hat{Y}_{sc} must coincide exactly with the ReNQSM redistribution operator,

$$\hat{Y}_{\text{sc}} = \hat{Y}_{\text{LS}}. \quad (81)$$

The time evaluation is formally described by

$$\hat{Y}_{\text{sc}}(t) = \mathcal{U}(t, -\infty) \hat{Y}_{\text{d}} \mathcal{U}^\dagger(t, -\infty), \quad (82)$$

but it is the many-body Hamiltonian ($H \equiv H(t=0)$) and the open-boundary conditions alone which determine the properties of this emerging Gibbs free energy. The formal time dependence is therefore limited to the adiabatic turn on itself,

$$\hat{Y}_{\text{sc}} \approx \hat{Y}_{\text{d}} + \exp(\eta t) [\hat{Y}_{\text{sc}}(t=0) - \hat{Y}_{\text{d}}]. \quad (83)$$

There is in steady state a cancellation of the time dependence in the creation and destruction operators in (82). As a consequence, the resulting Gibbs free energy is characterized by a time evolution

$$i \frac{d\hat{Y}_{\text{sc}}}{dt} \propto \eta, \quad (84)$$

which is identical to that derived for the steady-state electron redistribution operator \hat{Y}_{LS} derived and analyzed by Hershfield and Schiller [21, 22].

4.5. Total internal energy and state renormalization

When dealing with a fully time-dependent problem we obtain the exact total internal energy directly from the nonequilibrium density matrix solution

$$U_{\text{col}}(t) = \frac{\text{Tr}\{H\hat{\rho}_{\text{col}}(t)\}}{\text{Tr}\{\hat{\rho}_{\text{col}}(t)\}}. \quad (85)$$

This expression has just a trivial denominator, $\text{Tr}\{\hat{\rho}_{\text{col}}(t)\} = \text{Tr}\{\hat{\rho}_{\text{d}}\}$, because of the unitary character of the time-evolution operator, and the conserving nature of the nonequilibrium solution density matrix $\hat{\rho}_{\text{col}}(t)$.

It is instructive to discuss an apparent—but not actual—difference which arises in the evaluation of steady-state thermodynamic quantities depending on whether one retains the full nonequilibrium time dependence or whether one exploits the ReNEQSM (and the connection to the formal many-body LS solution via (3)). The apparent differences are most clearly evident in a discussion of a system-specific evaluation of the steady-state total internal energy,

$$U_{\text{LS}} = \frac{\text{Tr}\{H\hat{\rho}_{\text{LS}}\}}{\text{Tr}\{\hat{\rho}_{\text{LS}}\}}. \quad (86)$$

Because the solution density matrix $\hat{\rho}_{\text{LS}}$ commutes [21] with the fully interacting Hamiltonian (H), it is tempting (but wrong) to conclude that the set of initial $t \rightarrow -\infty$ disconnected equilibria eigenstates E_{ξ} provides a complete specification of U_{LS} .

For a steady-state tunneling problem there can be no difference between the formally exact evaluation (85) as a time-dependent problem and the also exact steady-state description (86). An apparent difference arises only because the formal many-body LS solution to the collision problem implies a projection (62) of the full dynamics onto the eigenstates of the ($t \approx 0$) Hamiltonian [123, 134, 136]. In a formal scattering theory description it is, of course, essential to include a description of both the level shifts [133, 134] and a possible collision-state renormalization [135, 136].

5. Variational nonequilibrium thermodynamic grand potential

The introduction provides a summary of the central enabling result of this paper, namely the description of the nature and properties of the exact nonequilibrium thermodynamic grand potential. Appendix C contains a formal proof of the variational properties, essentially adapting the analysis of Mermin [52]. Here I motivate and detail the recast of the exact QKA as a variational thermodynamic theory while also emphasizing central results.

5.1. Notation and motivation

The evaluation of expectation values (for a general operator $\hat{A}(t)$) is viewed as a functional

$$\langle \hat{A}(t) \rangle_{\hat{\rho}(t)} \equiv \frac{\text{Tr}\{\hat{\rho}(t)\hat{A}\}}{\text{Tr}\{\hat{\rho}(t)\}} \quad (87)$$

of a general nonequilibrium, time-dependent density matrix $\rho(t)$.

For a general nonequilibrium density matrix (electron distribution) there exists a natural functional evaluation of the entropy

$$S[\hat{\rho}(t)] = -\langle \ln \hat{\rho}(t) \rangle_{\hat{\rho}(t)} + \langle \ln[\text{Tr}\{\hat{\rho}(t)\}] \rangle_{\hat{\rho}(t)}. \quad (88)$$

Similarly, the evaluations of the nonequilibrium internal energies and Gibbs free energy,

$$U_{\text{col}}[\hat{\rho}(t)] = \langle H(t) \rangle_{\hat{\rho}(t)}, \quad (89)$$

$$Y_{\text{col}}[\hat{\rho}(t)] = \langle \hat{Y}_{\text{col}}(t) \rangle_{\hat{\rho}(t)}, \quad (90)$$

are set directly by the Hamiltonian $H(t)$ and by the emerging Gibbs free energy operator $\hat{Y}_{\text{col}}(t)$.

The nonequilibrium evaluations of entropy, internal energy, and Gibbs free energy functionals suggest, in turn, a functional form for the nonequilibrium grand potential as follows:

$$\Omega_{\text{col}}(t)[\hat{\rho}(t)] = -\frac{1}{\beta} S[\hat{\rho}(t)] + U_{\text{col}}[\hat{\rho}(t)] - Y_{\text{col}}[\hat{\rho}(t)]. \quad (91)$$

This expression is a generalization (2) of Mermin's (equilibrium) result to a nonequilibrium thermodynamic grand potential for collision problems. The formulation (91) is relevant for tunneling systems described by the continuum Caroli partition scheme.

For a compact presentation of derivatives and forces it is convenient to view the nonequilibrium thermodynamic grand potential functional (2) as a special (collision) instance of the more general functional

$$\Omega_{\tilde{X}(t)}[\rho(t)] \equiv \langle \tilde{X}(t) + \beta^{-1} \ln \hat{\rho}(t) - \beta^{-1} \ln[\text{Tr}\{\hat{\rho}(t)\}] \rangle_{\hat{\rho}(t)}. \quad (92)$$

Obviously, it holds that

$$\Omega_{\text{col}}[\hat{\rho}(t)] = \Omega_{\tilde{X}(t) \equiv H(T) - \hat{Y}_{\text{col}}(t)}[\hat{\rho}(t)]. \quad (93)$$

5.2. Variational thermodynamics

A simple generalization of Mermin's analysis (appendix C) demonstrates that the nonequilibrium thermodynamic grand potential (2) is extremal at the exact nonequilibrium collision density matrix $\hat{\rho}_{\text{col}}(t)$,

$$\Omega_{\text{col}}[\hat{\rho}(t)] > \Omega_{\text{col}}[\hat{\rho}_{\text{col}}(t)] = \Omega_{\text{col}}(t). \quad (94)$$

That is, the grand potential functional acquires the expected minimum (1) as the extremal value and thus serves both to identify the exact nonequilibrium grand potential value (1) and the exact nonequilibrium density matrix for interacting tunneling problems. A Mermin-type variational principle (94) for nonequilibrium thermodynamic theory is, of course, expected given the ReNQSM nature, i.e., the reformulation of nonequilibrium tunneling as an effective equilibrium statistical mechanics problem [21–27]. The (generalized) Mermin thermodynamic variational principle [17, 52] supplements the ground state, action and many-body LS T -matrix principles. Variational principles are indispensable in DFT formulations.

The variational property (94) is proved (in appendix C) for members, $\hat{\rho}$, of the class of normalized nonequilibrium density matrices with a statistical weighting given by a Hermitian operator $\hat{X}(t)$ and normalization $N_{\hat{X}(t)}$,

$$\hat{\rho} \in \{N_{\hat{X}(t)}\hat{\rho}_{\hat{X}(t)}\}, \quad (95)$$

$$\hat{\rho}_{\hat{X}(t)} \equiv \exp[-\beta\hat{X}(t)], \quad (96)$$

$$N_{\hat{X}(t)} = \text{Tr}\{\hat{\rho}_{\hat{X}(t)}\}. \quad (97)$$

The conservative nature of the QKA is, of course, sufficient to ensure that the normalization is independent of time; when using the formal many-body LS solution for steady-state problems one must explicitly ensure normalizations [134–136].

The density matrix class $\{N_{\hat{X}(t)}\hat{\rho}_{\hat{X}(t)}\}$ encompasses all possible nonequilibrium density matrices $\hat{\rho}_{\text{col}}(t)$ that emerge (with conserving dynamics) in a general collision problem, equations (70) and (71). The extremal property is therefore sufficient to uniquely identify the correct nonequilibrium collision density matrix (66) for a given (interacting) tunneling problem specified as continuum Caroli partition scheme.

From the Mermin-type analysis one immediately finds a stationary property of

$$\Omega_{\hat{X}(t)} \equiv \Omega_{\hat{X}(t)}[\hat{\rho}_{\hat{X}(t)}], \quad (98)$$

which can be formulated from the functional expression

$$\begin{aligned} \left. \frac{\partial \Omega_{\hat{X}_0(t)+\lambda\hat{\Delta}(t)}}{\partial \lambda} \right|_{\lambda=0} &= \left\langle \left. \frac{\partial \hat{\rho}_{\hat{X}_0(t)+\lambda\hat{\Delta}(t)}}{\partial \lambda} \right|_{\lambda=0} \right\rangle_{\hat{\rho}_{\hat{X}_0(t)}} \\ &= \langle \hat{\Delta}(t) \rangle_{\hat{\rho}_{\hat{X}_0(t)}}. \end{aligned} \quad (99)$$

As in the corresponding equilibrium case [52], this property is central to demonstrating the variational and extremal properties of the thermodynamic grand potential at the solution density matrix $\hat{\rho}_{\text{col}}(t)$.

5.3. Extremal property as a tempered maximization of entropy

The nonequilibrium solution density matrix $\hat{\rho}_{\text{col}}(t)$ is unique and can be identified by the minimum of the variational thermodynamic grand potential functional. From the construction of the thermodynamic potential it follows that

$$\begin{aligned} \frac{1}{\beta} \frac{\delta}{\delta \hat{\rho}} S[\hat{\rho}] &= -\frac{\delta}{\delta \hat{\rho}} \{ \Omega_{\text{col}}(t)[\hat{\rho}] \\ &\quad - (U_{\text{col}}(t)[\hat{\rho}] - Y_{\text{col}}(t)[\hat{\rho}]) \}, \end{aligned} \quad (100)$$

and that, following a system perturbation, $\hat{\rho}(t) \neq \hat{\rho}_{\text{col}}(t)$, we expect a relaxation because it corresponds to a maximization of electron entropy. This maximization is naturally limited or tempered by a functional for the total internal energy and Gibbs free energy difference, $U_{\text{col}}(t)[\hat{\rho}] - Y_{\text{col}}(t)[\hat{\rho}]$.

The maximum entropy character of the here-presented theory makes it clear that there are close relations to the range of constrained maximum entropy formulations [29–31]. However, there are also important differences. While the

constrained maximum entropy approaches use Lagrange multipliers to specify selected expectation values (for example, the current flow), the explicit need for constraints is bypassed in the ReNQSM and in this variational thermodynamic description. Specifically, I stress that the approach does not impose a value for the internal energy or Gibbs free energy and that $U_{\text{col}}(t)[\hat{\rho}] - Y_{\text{col}}(t)[\hat{\rho}]$ is itself uniquely specified by the boundary conditions and by the actual time evolution.

5.4. Generalized Hellmann–Feynman theorem

The fact that the exact nonequilibrium solution can be viewed as a maximization of entropy provides a rationale for introducing generalized thermodynamic forces

$$\mathbf{F}_{\text{col},\hat{\rho}}^{\text{GCE}} \equiv -\frac{\partial}{\partial \hat{\rho}} \Omega_{\text{col}}(t)[\hat{\rho}]. \quad (101)$$

The more specific thermodynamic force definition

$$\mathbf{F}_{\text{col},\mathbf{R}_i}^{\text{GCE}}(t) \equiv -\frac{\partial}{\partial \mathbf{R}_i} \Omega_{\text{col}}(t) \quad (102)$$

is given by a parametric dependence of the density matrix (as will be further motivated for steady-state problems in section 6). The combined electron–nucleus system is here simply assumed to further the maximization of the entropy content (in the electron system).

A generalized Hellmann–Feynman theorem exists to simplify the determination of such thermodynamic forces, here as discussed for time-dependent tunneling. As an explicit expression of (99), one can specify the perturbation

$$\hat{\Delta}(t) = \frac{\partial}{\partial \mathbf{R}_i} \hat{X}_{\text{col}}(t) \cdot \delta \mathbf{R}_i \quad (103)$$

and evaluate the changes corresponding to a derivative of the thermodynamic potential along a coordinate-line element $\delta \mathbf{R}_i$,

$$\delta \mathbf{R}_i \cdot \frac{\partial}{\partial \mathbf{R}_i} \Omega_{\text{col}}(t) = \delta \mathbf{R}_i \cdot \left\langle \frac{\partial \hat{X}_{\text{col}}}{\partial \mathbf{R}_i} \right\rangle_{\hat{\rho}=\hat{\rho}_{\text{col}}(t)}. \quad (104)$$

This provides a demonstration of a nonequilibrium generalized Hellmann–Feynman,

$$\frac{\partial}{\partial \mathbf{R}_i} \Omega_{\text{col}}(t) = \left\langle \frac{\partial}{\partial \mathbf{R}_i} [H(t) - \hat{Y}_{\text{col}}(t)] \right\rangle_{\hat{\rho}_{\text{col}}(t)}, \quad (105)$$

for a thermodynamic description of tunneling.

6. Steady-state thermodynamics and adiabatic transformations

The formulation in terms of a nonequilibrium grand potential functional (above) is by construction fully equivalent to the exact solution in the QKA [15]. This formal result can also be used to investigate tunneling described by a time-independent potential and subject to the assumption that a steady-state solution (described by the many-body LS equation) has emerged. There does exist an argument that a steady-state

solution will emerge under general conditions¹⁶ [23]. The following steady-state analysis provides a framework for a discussion of adiabatic relaxations and a nonequilibrium Born–Oppenheimer approximation.

6.1. State functions for steady-state tunneling

If all nuclei coordinates are changed at an infinitely slow rate along a given deformation path, it follows that the system can always be assumed to be described by the exact steady-state density matrix solution $\hat{\rho}_{\text{LS}}(\{\mathbf{R}_i\})$. As indicated, this solution is then a function of the set of classical-coordinate values as they vary along the deformation path. The density matrix solution specifies in turn an exact evaluation of corresponding thermodynamics state functions

$$\bar{U}_{\text{LS}}(\mu_{\text{L}}, \mu_{\text{R}}; \{\mathbf{R}_i\}) \equiv U_{\text{LS}}[\hat{\rho}_{\text{LS}}], \quad (106)$$

$$\bar{Y}_{\text{LS}}(\mu_{\text{L}}, \mu_{\text{R}}; \{\mathbf{R}_i\}) \equiv Y_{\text{LS}}[\hat{\rho}_{\text{LS}}], \quad (107)$$

$$\bar{S}_{\text{LS}}(\mu_{\text{L}}, \mu_{\text{R}}; \{\mathbf{R}_i\}) \equiv S[\hat{\rho}_{\text{LS}}], \quad (108)$$

$$\bar{\Omega}_{\text{LS}}(\mu_{\text{L}}, \mu_{\text{R}}; \{\mathbf{R}_i\}) \equiv \Omega_{\text{LS}}[\hat{\rho}_{\text{LS}}], \quad (109)$$

namely for the internal energy, for the Gibbs free energy, for the entropy and for the nonequilibrium grand potential, respectively.

6.2. Steady-state thermodynamic forces

From the state functions and using the generalized Hellmann–Feynman of the variational nonequilibrium thermodynamic theory, one immediately obtains the thermodynamic forces

$$\mathbf{F}_{\text{LS}, \mathbf{R}_i}^{\text{GCE}} \equiv -\frac{\partial}{\partial \mathbf{R}_i} \bar{\Omega}_{\text{LS}}(\mu_{\text{L}}, \mu_{\text{R}}; \{\mathbf{R}_i\}). \quad (110)$$

I find (as expected) that the GCE conditions invalidate a traditional Hellmann–Feynman evaluation,

$$\begin{aligned} \frac{\partial}{\partial \mathbf{R}_i} \bar{U}_{\text{LS}} &= \left\langle \frac{\partial H}{\partial \mathbf{R}_i} \right\rangle_{\hat{\rho}_{\text{LS}}} \\ &+ \frac{\text{Tr}\{(H - \bar{U}_{\text{LS}}) \frac{\partial}{\partial \mathbf{R}_i} e^{-\beta(H - \hat{Y}_{\text{LS}})}\}}{\text{Tr}\{e^{-\beta(H - \hat{Y}_{\text{LS}})}\}} \end{aligned} \quad (111)$$

$$\neq \left\langle \frac{\partial}{\partial \mathbf{R}_i} H \right\rangle_{\hat{\rho}_{\text{LS}}}. \quad (112)$$

There is a corresponding complication in a GCE evaluation of the Gibbs free energy,

$$\begin{aligned} \frac{\partial}{\partial \mathbf{R}_i} \bar{Y}_{\text{LS}} &= \left\langle \frac{\partial \hat{Y}_{\text{LS}}}{\partial \mathbf{R}_i} \right\rangle_{\rho_{\text{LS}}} \\ &+ \frac{\text{Tr}\{(\hat{Y}_{\text{LS}} - \bar{Y}_{\text{LS}}) \frac{\partial}{\partial \mathbf{R}_i} e^{-\beta(H - \hat{Y}_{\text{LS}})}\}}{\text{Tr}\{e^{-\beta(H - \hat{Y}_{\text{LS}})}\}} \end{aligned} \quad (113)$$

¹⁶Tunneling in a system described by a time-independent scattering potential need not always have stationary electron dynamics. As also discussed in [64], a time-dependent tunneling behavior can arise through an intermittent behavior, for example, in an ordinary avalanche diode.

$$\neq \left\langle \frac{\partial}{\partial \mathbf{R}_i} \hat{Y}_{\text{LS}} \right\rangle_{\hat{\rho}_{\text{LS}}} \quad (114)$$

and the exact steady-state generalized Hellmann–Feynman force description (110) arises only upon cancellations.

The steady-state thermodynamic forces (110) are useful as they serve to trace out changes in the thermodynamic grand potential value among different possible nuclei configurations as well as concerted changes in other extensive thermodynamic functionals, equation (106)–(108). I also stress that integrating the thermodynamic grand potential changes from the force expression (110)—and using the extremal character of the thermodynamic grand potential—will in turn uniquely identify the solution nonequilibrium density matrix at the final coordinates. Section 6.4 contains an argument for using these steady-state thermodynamic forces in a nonequilibrium Born–Oppenheimer approximation.

6.3. Relation to electrostatic forces

I observe that the thermodynamics forces (110) are formally different from the electrostatic forces often used in nonequilibrium studies. By a natural assumption of ergodicity it follows that the steady-state description must also reflect fluctuations [70–72] and that the tunneling systems must be treated as a statistical ensemble (even at $\beta \rightarrow 0$). Electrostatic forces will only be interesting in the context of a GCE thermodynamics if (6) provides an evaluation which is representative for this ensemble. However, the source of an additional force contribution with a statistical origin (for example, the electron redistribution effects arising in open systems [21, 22, 24, 147]) is directly evident in the exact ReNQSM result for an effective (unnormalized) steady-state nonequilibrium density matrix [21] (53). This exact nonequilibrium density matrix depends on the operator \hat{Y}_{LS} for interaction-induced redistributions of electrons, i.e., the emerging Gibbs free energy operator. Accordingly, it is important that the forces that effectively act on this ensemble (of steady-state nonequilibrium tunneling systems) reflect the sensitivity of this electron redistribution to the nuclei positions¹⁷.

In a GCE thermodynamic description, the classical nuclei still respond partly to electrostatic forces but the adiabatic relaxations (of classical nuclei) will also reflect a tendency to seek thermodynamically favorable electron distributions [21]; these distribution changes are specified in part by a correct evaluation of the Gibbs free energy effects. The analysis of [21] shows that there is no change in the Gibbs free energy operator \hat{Y}_{LS} in equilibrium. However, that does not generally apply under general nonequilibrium conditions where the operator $\hat{N}_{\text{L(R)}}$ for counting particles in either lead can no longer be treated as a conserved property. An assumption that $\partial \hat{Y}_{\text{LS}} / \partial \mathbf{R}_i$ vanishes would significantly

¹⁷The steady-state ReNQSM [21, 131] contains an explicit construction of the operator \hat{Y}_{LS} order-by-order in the perturbation term (that includes the external potential). This construction strongly suggests that it is essential to retain an explicit dependence on the nuclei positions in the resulting operator \hat{Y}_{LS} (under nonequilibrium conditions).

simplify the formulation of density functionals (section 7) but such an assumption is not motivated by the steady-state ReNQSM [21].

I also observe that the Green function framework (section 2.2 and appendix A) and the S -matrix framework (section 2.2 and appendix B) for calculations of finite-bias noninteracting thermodynamics suggest that we must generally expect differences in the electrostatic and thermodynamic forces. Appendix A provides a formal nonequilibrium Green function demonstration that the exact adiabatic thermodynamic forces (110) do reduce to GCE electrostatic forces when the changes in the full electron distribution are completely specified by the changes in the full density of states. However, that is an assumption which does not generally hold outside equilibrium (for example as discussed in [37, 41, 42]).

Similarly, an S -matrix analysis (appendix B) links the electrostatic forces and the thermodynamic forces to two different components of a scattering phase-shift characterization. An assumption that changes in the full density of states determine the full electron distribution implies that the GCE thermodynamic potential is specified by

$$\Delta \mathcal{N}_{\text{tot}}(\omega) = \frac{2}{\pi} [\delta_{\text{L}}^{\text{eff}}(\omega) + \delta_{\text{L}}^{\text{eff}}(\omega)] \equiv \frac{2}{\pi} \delta_{\text{tot}}^{\text{eff}}(\omega). \quad (115)$$

The partial-pressure determination [148] of the nonequilibrium systems yields instead lead-specific thermodynamic grand potential components given by $\delta_{\text{L}}^{\text{eff}}(\omega)$ for $\mu_{\text{L}} \gg \mu_{\text{R}}$. Appendix B contains an example analysis for a one-dimensional transport description, based on [144]. In this model study one can identify the lead-projected (full, unprojected) phase-shift component $\delta_{\text{L}}^{\text{eff}}(\omega)$ ($\delta_{\text{tot}}^{\text{eff}}(\omega)$) as the phase shift for free-particle reflection into the emitter lead (transmission into the collector). There is no general nature of the S -matrix behavior which would ensure equivalence of thermodynamic forces (given by the reflection phase shift) and electrostatic forces (given by the transmission phase shift).

There are thus several arguments for a formal and actual difference between thermodynamic and electrostatic forces under nonequilibrium conditions (beyond linear response). The most important argument for a difference is, of course, the following fact: while there are arguments for a nonconservative nature of the electrostatic forces, this paper shows that the adiabatic thermodynamic forces will always remain explicitly conservative.

6.4. Nature of the steady-state adiabatic forces

The steady-state thermodynamic forces (110) (like the general variation grand potential) express a controlled entropy maximization

$$\frac{1}{\beta} \frac{\delta}{\delta \hat{\rho}} S[\hat{\rho}] = -\frac{\delta}{\delta \hat{\rho}} \{ \Omega_{\text{LS}}[\hat{\rho}] - (U_{\text{LS}}[\hat{\rho}] - Y_{\text{LS}}[\hat{\rho}]) \}. \quad (116)$$

The optimization arises subject to rigorous boundary conditions, namely, the QKA results for the internal energy and Gibbs free energy contents. This suggests an intrinsic value for modeling relaxations.

One can, for example, use the exact thermodynamic forces (110) to discuss the thermodynamic stability of a steady-state tunneling system in the limit of infinitely slow deformations. The initial state (before the transformation around a loop) is uniquely characterized by the solution density matrix $\hat{\rho}_{\text{LS}}$ and potential value $\bar{\Omega}_{\text{LS}}$. Following any transformation around a closed loop we will in general obtain a new density matrix $\hat{\rho}^f$ and a new thermodynamic potential value $\bar{\Omega}_{\text{LS}}^f$. However, with the underlying state function assumption of infinitely slow deformation it follows that $\bar{\Omega}_{\text{LS}}^f = \Omega_{\text{LS}}[\hat{\rho}^f] = \bar{\Omega}_{\text{LS}}$, and that we must have returned to the exact same density matrix, $\hat{\rho}^f \equiv \hat{\rho}_{\text{LS}}$. Not surprisingly, the conserving nature of the thermodynamic forces ensures that all state functions must attain exactly the same values as the initial state functions,

$$\delta \bar{S}_{\text{LS}} = \delta \bar{U}_{\text{LS}} = \delta \bar{Y}_{\text{LS}} = \delta \bar{\Omega}_{\text{LS}} \equiv 0. \quad (117)$$

Appendix E provides additional formal results on relations among variations of the set of thermodynamic state functions.

The extremal property of $\bar{\Omega}_{\text{LS}}$ ensures, in fact, that the exact steady-state thermodynamic forces (110) are inherently adiabatic in nature, i.e., valid and needed in the limit where we can assume an infinite ratio of the nucleus-to-electron masses. This adiabatic nature follows because a sufficiently slow implementation will automatically avoid all thermodynamic excitations.

The basis in a physics principle and the automatic ability to avoid all thermodynamic excitations suggest that the here-derived conservative thermodynamic forces are well suited for use in a nonequilibrium Born–Oppenheimer approximation.

7. Variational thermodynamics for noninteracting tunneling

This paper develops a DFT formulation with a corresponding SP framework for efficient computations. This involves a self-consistency loop where SP determinations of the electron density are used to update the universal functional description. It is therefore important to demonstrate that effective SP calculations (of the density) are uniquely defined within the (full nonequilibrium interacting) variational thermodynamic theory.

7.1. The independent-particle dynamics

For noninteracting particles, described by the quadratic Hamiltonian $H_{\text{V}}^{(0)}$, it is clear that the set of SP LS solutions [22]

$$|\psi_{\text{LS},\lambda_p}^{(0)}\rangle = (\hat{\psi}_{\text{LS},\lambda_p}^{(0)})^\dagger |0\rangle, \quad (118)$$

$$(\hat{\psi}_{\text{LS},\lambda_p}^{(0)})^\dagger = \frac{i\eta}{\epsilon_{\lambda_p} + \mathcal{L}_{H_{\text{V}}^{(0)}} + i\eta} \quad (119)$$

coincides with the SP LS solutions introduced and discussed in section 2 and in appendix A. It is also clear that these SP LS states constitute the basis of what is formally the many-body

solution for a steady-state tunneling problem [21–27, 131, 157]. The states (118) express the (steady-state) solution that emerges from an initial H_d eigenstate $|\phi_{\lambda_p}\rangle$ in formal LS collision theory [138]. There can be a finite shift [134] of the energy ϵ_{λ_p} if the perturbation introduces an infinitely extended periodic potential [133, 135]; as always in formal scattering theory, there will be infinitesimal energy shifts leading to changes in the integrated density of states [147, 152, 153] that are stipulated by the Friedel sum rule [130]. I do not (yet) express these energy shifts so as to keep the nomenclature simple in the following analysis.

The states and the their creation operators, (118) and (119), retain a genuine independent-particle nature and hence the emerging Gibbs free energy, denoted $\hat{Y}_V^{(0)}$, is also quadratic. It is also clear that these SP solutions must enter both the nonequilibrium solution density matrix and the thermodynamic value. In particular, it is possible to obtain a separable form of the nonequilibrium solution density matrix

$$\hat{\rho}_{LS}^{(0)} = \Pi_{\lambda_p} \hat{\rho}_{LS,\lambda_p}^{(0)}, \quad (120)$$

$$\hat{\rho}_{LS,\lambda_p}^{(0)} = \exp[-\beta(\epsilon_{\lambda_p} - \mu_p) \hat{n}_{\lambda_p}], \quad (121)$$

$$\hat{n}_{\lambda_p} = (\hat{\psi}_{LS,\lambda_p}^{(0)})^\dagger \hat{\psi}_{LS,\lambda_p}^{(0)}, \quad (122)$$

and of the corresponding nonequilibrium thermodynamic grand potential.

7.2. Variational link to the single-particle Lippmann–Schwinger solution

For noninteracting transport it is sufficient to limit the variational space (for the nonequilibrium solution density matrix) to that produced by a corresponding set of mutually orthogonal trial functions $\tilde{\psi}_{\lambda_p}(\mathbf{r}) = \langle \mathbf{r} | \tilde{\psi}_{\lambda_p} \rangle$. These trial functions approximate the form of an SP scattering state from H_d eigenstates of energy ϵ_{λ_p} . No assumption is made for the normalization of these trial scattering wavefunctions whereas

I use $\{\hat{\psi}_{\lambda_p}^\dagger\}$ to denote creation operators for such states with a suitable standard (delta-function) normalization

$$\hat{\psi}_{\lambda_p}^\dagger |0\rangle = \frac{|\tilde{\psi}_{\lambda_p}\rangle}{\langle \tilde{\psi}_{\lambda_p} | \tilde{\psi}_{\lambda_p} \rangle^{1/2}}. \quad (123)$$

I also introduce $\hat{n}_{\lambda_p} = \tilde{\psi}_{\lambda_p}^\dagger \tilde{\psi}_{\lambda_p}$ and define the trial density matrix solution

$$\hat{\rho} = \Pi_{\lambda_p} \hat{\rho}_{\lambda_p}, \quad (124)$$

$$\begin{aligned} \hat{\rho}_{\lambda_p} &= \exp[-\beta(\epsilon_{\lambda_p} - \mu_p) \hat{n}_{\lambda_p}], \\ &= 1 + \hat{n}_{\lambda_p} (\exp[-\beta(\epsilon_{\lambda_p} - \mu_p)] - 1). \end{aligned} \quad (125)$$

I note that the difference between the internal and Gibbs free energies is an SP operator which can be expressed in terms of the trial wavefunctions

$$\begin{aligned} H_V^{(0)} - \hat{Y}_V^{(0)} &= \sum_{\lambda',p'} \sum_{\lambda_p} \frac{\langle \tilde{\psi}_{\lambda',p'} | (H_V^{(0)} - \hat{Y}_V^{(0)}) | \tilde{\psi}_{\lambda_p} \rangle}{\langle \tilde{\psi}_{\lambda',p'} | \tilde{\psi}_{\lambda',p'} \rangle^{1/2} \langle \tilde{\psi}_{\lambda_p} | \tilde{\psi}_{\lambda_p} \rangle^{1/2}} \\ &\quad \times \hat{\psi}_{\lambda',p'}^\dagger \hat{\psi}_{\lambda_p}. \end{aligned} \quad (126)$$

The variational form of the grand potential value is also separable,

$$\Omega_V^{(0)}[\hat{\rho}] = \sum_{\lambda_p} \Omega_{V,\lambda_p}^{(0)}[\hat{\rho}_{\lambda_p}], \quad (127)$$

$$\Omega_{V,\lambda_p}^{(0)}[\hat{\rho}_{\lambda_p}] = \Omega_{V,\lambda_p}^{(0)} + \Delta\Omega_{V,\lambda_p}^{(0)}[\hat{\rho}_{\lambda_p}], \quad (128)$$

$$\begin{aligned} \Omega_{V,\lambda_p}^{(0)} &= -\frac{1}{\beta} \ln \text{Tr}\{\hat{\rho}_{\lambda_p}\} \\ &= -\frac{1}{\beta} \ln(1 + \exp[-\beta(\epsilon_{\lambda_p} - \mu_p)]), \end{aligned} \quad (129)$$

$$\Delta\Omega_{V,\lambda_p}^{(0)}[\hat{\rho}_{\lambda_p}] = \frac{\text{Tr}\{\hat{\rho}_{\lambda_p}[H_V^{(0)} - \hat{Y}_V^{(0)} + (1/\beta) \ln(\hat{\rho}_{\lambda_p})\]}}{\text{Tr}\{\hat{\rho}_{\lambda_p}\}}. \quad (130)$$

I observe that the components of the grand-canonical potential functional have the minimum

$$\Omega_{V,\lambda_p}^{(0)}[\hat{\rho}_{\lambda_p} = \hat{\rho}_{LS,\lambda_p}] = \Omega_{V,\lambda_p}^{(0)}. \quad (131)$$

Below, in the spirit of [160], I investigate the SP thermodynamics by considering the variational contributions from each of the orthogonal trial scattering eigenstates, $\{\lambda_p\}$, at a time.

It is straightforward to evaluate the terms in the variational separable grand potential functional,

$$\Delta\Omega_{V,\lambda_p}^{(0)}[\hat{\rho}] = (\epsilon_{\lambda_p} - \mu_p) \langle \hat{n}_{\lambda_p} \rangle_{\hat{\rho}_{\lambda_p}} (C[\tilde{\psi}_{\lambda_p}] - 1), \quad (132)$$

$$C[\tilde{\psi}_{\lambda_p}] = \frac{\langle \tilde{\psi}_{\lambda_p} | (H_V^{(0)} - \hat{Y}_V^{(0)}) | \tilde{\psi}_{\lambda_p} \rangle}{(\epsilon_{\lambda_p} - \mu_p) \langle \tilde{\psi}_{\lambda_p} | \tilde{\psi}_{\lambda_p} \rangle}, \quad (133)$$

$$\begin{aligned} \langle \hat{n}_{\lambda_p} \rangle_{\hat{\rho}_{\lambda_p}} &= \frac{\text{Tr}\{\hat{\rho}_{\lambda_p} \hat{n}_{\lambda_p}\}}{\text{Tr}\{\hat{\rho}_{\lambda_p}\}} \\ &= \frac{\exp[-\beta(\epsilon_{\lambda_p} - \mu_p)]}{1 + \exp[-\beta(\epsilon_{\lambda_p} - \mu_p)]} \\ &= \langle \hat{n}_{\lambda_p} \rangle_{\hat{\rho}_{LS}^{(0)}}. \end{aligned} \quad (134)$$

It follows that the variational nature of the nonequilibrium thermodynamic grand potential can be expressed as

$$\frac{\delta\Omega_V^{(0)}[\hat{\rho}]}{\delta\tilde{\psi}_{\lambda_p}^*(\mathbf{r})} = \frac{\delta\Omega_{V,\lambda_p}^{(0)}[\hat{\rho}_{\lambda_p}]}{\delta\tilde{\psi}_{\lambda_p}^*(\mathbf{r})} = 0, \quad (135)$$

$$\begin{aligned} D[\tilde{\psi}_{\lambda_p}]^{-1} \frac{\delta\Omega_{V,\lambda_p}^{(0)}[\hat{\rho}_{\lambda_p}]}{\delta\tilde{\psi}_{\lambda_p}^*(\mathbf{r})} &= \langle \mathbf{r} | (H_V^{(0)} - \hat{Y}_V^{(0)}) | \tilde{\psi}_{\lambda_p} \rangle \\ &\quad - C[\tilde{\psi}_{\lambda_p}] (\epsilon_{\lambda_p} - \mu_p) \langle \mathbf{r} | \tilde{\psi}_{\lambda_p} \rangle, \end{aligned} \quad (136)$$

$$D[\tilde{\psi}_{\lambda_p}] = \frac{\langle \hat{n}_{\lambda_p} \rangle_{\hat{\rho}_{LS}^{(0)}}}{\langle \tilde{\psi}_{\lambda_p} | \tilde{\psi}_{\lambda_p} \rangle}. \quad (137)$$

Since $C[\tilde{\psi}_{\lambda_p}] = 1$ (at the solution), it is possible to express the variational condition (136) simply as the condition

$$(H_V^{(0)} - \hat{Y}_V^{(0)}) | \tilde{\psi}_{\lambda_p} \rangle = (\epsilon_{\lambda_p} - \mu_p) | \tilde{\psi}_{\lambda_p} \rangle. \quad (138)$$

This equation is obviously solved by the formal SP LS solution, (118) and (119).

7.3. Calculation of single-particle properties

From the variational thermodynamic description of the noninteracting particles we can represent the full variation of the noninteracting Green functions and expectation values of all SP operators. I exemplify this computational power with a determination of the electron-density variation.

The initial disconnected system is fully characterized through the retarded Green function operator $\hat{g}_r^d(\omega) = \sum_{J=L/R/C} \hat{g}_r^{dJ}(\omega)$, given by equations (A.1) and (A.2), and by the initial electron occupation. Analytic properties relate the retarded and advanced Green functions ($\hat{g}_a(\omega) = \hat{g}_r^*(\omega)$) and permit a simple expression also of the disconnected equilibria spectral function (A.4). Each of the separate sections is equilibrium and the initial system is thus described by an electron distribution or less-than Green function operator [13],

$$\begin{aligned} \hat{g}_<^d(\omega) &= \hat{g}_{<,\mu=\mu_J}^{dJ=L/R/C}(\omega), & (139) \\ \hat{g}_{<,\mu}^{dJ}(\omega) &= f_\mu(\omega) i [\hat{g}_r^{dJ}(\omega) - \hat{g}_a^{dJ}(\omega)] \\ &= f_\mu(\omega) \sum_{\lambda_J} |\lambda_J\rangle \langle \lambda_J| \delta(\omega - \epsilon_{\lambda_J}). & (140) \end{aligned}$$

Here ‘ λ_J ’ identifies an eigenstate of energy ϵ_{λ_J} which resides in the leads or in the center. This definition is consistent with the one introduced and used in section 2.2. I have in (140) chosen to explicitly state the dependence on the (lead-specific) chemical potential, to stress the relation with the formulation in [148].

After the adiabatic turn on we have the system described by the SP LS solutions (118). The retarded Green function for the connected noninteracting system $H^{(0)}$ is given by the Dyson equation [132] as well as a formal Green function evaluation based on an analysis [134] of the (SP) LS solution,

$$\hat{g}_r^{(0)}(\omega) = \sum_{P=L/R} \hat{g}_r^{(0),P}(\omega), \quad (141)$$

$$\hat{g}_r^{(0),P}(\omega) = \sum_{\lambda} \frac{|\psi_{LS,\lambda p}^{(0)}\rangle \langle \psi_{LS,\lambda p}^{(0)}|}{\omega - \tilde{\epsilon}_{\lambda,p} + i\eta}. \quad (142)$$

The scattering-state poles $\tilde{\epsilon}_{\lambda p}$ are given by infinitesimal level shifts relative to original disconnected-system eigenvalues $\epsilon_{\lambda p}$. The formulation (141) applies in transport cases when we can ignore bound states [134, 135]. I will not consider possible charging-hysteresis cases here [46].

From the formal scattering theory results there is also a link to a full nonequilibrium Green function determination for noninteracting particles. The Green-theorem boundary terms enter in the evaluation of the operator for the noninteracting less-than Green function,

$$\hat{g}_<^{(0)}(\omega) = \sum_{P=L/R} [1 + \hat{g}_r^{(0)}(\omega) H_{1,V}^{(0)}] \hat{g}_<^P(\omega) [1 + H_{1,V}^{(0)} \hat{g}_a^{(0)}(\omega)]. \quad (143)$$

Inserting (140) in (143) yields

$$\hat{g}_<^{(0)}(\omega) = \sum_{P=L/R} \hat{g}_{<,\mu'=\mu_P}^{(0),P}(\omega), \quad (144)$$

$$\hat{g}_{<,\mu'}^{(0),P}(\omega) = 2\pi f_{\mu'}(\omega) \sum_{\lambda_P} |\psi_{LS,\lambda p}^{(0)}\rangle \langle \psi_{LS,\lambda p}^{(0)}| \delta(\omega - \tilde{\epsilon}_{\lambda p}), \quad (145)$$

a sum where each term corresponds exactly to the contribution from the individual (independent) SP LS solution. Again the description here is consistent with that used in section 2.3. The connection between the SP LS solutions and the noninteracting Green functions is, of course, well known.

To calculate many SP properties it is practical to seek a real-space representation; here we exemplify a determination of the electron-density variation in tunneling. From the SP LS solutions, expressed through (143), one defines

$$g_{<}^{(0)}(\mathbf{r}, \mathbf{r}', \omega) \equiv \langle \mathbf{r} | \hat{g}_<^{(0)}(\omega) | \mathbf{r}' \rangle, \quad (146)$$

and one immediately obtains a determination of, for example, the electron-density variation

$$n(\mathbf{r}) = \int d\omega g_{<}^{(0)}(\mathbf{r}, \mathbf{r}, \omega). \quad (147)$$

It is sometimes natural to contrast this density variation with the corresponding result $n^d(\mathbf{r})$ for the initial, disconnected system and consider

$$\Delta n(\mathbf{r}) = n(\mathbf{r}) - n^d(\mathbf{r}). \quad (148)$$

For simple model systems defined by a double-barrier structure the tunneling-induced density change (148) includes a variation in nonequilibrium resonant level charging [42, 46] and nonequilibrium Friedel density oscillations¹⁸. With a true noninteracting-electron modeling (i.e., in the absence of actual many-body scattering) the electron-density change $\Delta n(\mathbf{r})$ also includes a position-independent component which corresponds to SP transmission.

The robust SP LS solver strategies employed in standard DBT codes [118–122] excel at calculation of the density variation (147) for any given SP potential. Calculation of the effective density variation (148) is, of course, a core step also in an exact nonequilibrium thermodynamic DFT.

8. Density functional theory of interacting tunneling

The Mermin-type proof of the variational property equation (94) of the nonequilibrium grand potential does not require, nor by itself provide, uniqueness of density in nonequilibrium tunneling. This is in contrast to the case of thermal properties in equilibrium [52]. Nevertheless, the previously formulated LS collision DFT [64] and open-system time-dependent DFT analysis [161] still provide a proof for uniqueness of density for collision problems, appendix D.

The uniqueness of density proof is here used to define an SP formulation for exact calculations of interacting nonequilibrium thermodynamics based on universal energy functionals. The formally exact theory contains the set of DBT descriptions as a first consistent but also un-quantified

¹⁸ The Friedel density oscillations are very pronounced in studies of tunneling in two-dimensional systems and evident, for example, in figure 10 of the first article listed in [121] and figure 2 of the second article listed in [121].

approximation. The here-presented thermodynamic DFT provides a formal framework for systematic improvements beyond DBT.

8.1. Uniqueness of density in nonequilibrium thermodynamics

The unitary evolution provides an explicit construction for the mapping

$$\mathcal{N} : v_{\text{col}}(\mathbf{r}, t) \longrightarrow n(\mathbf{r}, t) = \langle \hat{n}(\mathbf{r}) \rangle_{\text{col}}(t). \quad (149)$$

The LS collision DFT proof for uniqueness of density [64] explores the time evolution in the collision picture to prove that \mathcal{N} is unique, i.e., that for every $v_{\text{col}}(\mathbf{r}, t)$ there can be at most one time-dependent density. Also, the case of steady-state tunneling resulting from the adiabatic turn on is just a particular form of time-dependent behavior and the uniqueness of density extends also to cases where the collision term reduces to a time-independent scattering potential $v_{\text{sc}}(\mathbf{r})$. Under the assumption that a steady-state behavior emerges from $v_{\text{sc}}(\mathbf{r})$ the mapping \mathcal{N} is then instead completely described by the steady-state density matrix (53),

$$\mathcal{N} : v_{\text{sc}}(\mathbf{r}) \longrightarrow n(\mathbf{r}) = \langle \hat{n}(\mathbf{r}) \rangle_{\text{sc}}. \quad (150)$$

It follows either by the boundary conditions discussed in [21] or directly by differentiating the mapping (149) that the resulting density can have no more than an adiabatic time dependence, $n(\mathbf{r}, t) \sim n(\mathbf{r}) \exp(\eta t)$.

This unique mapping between density and external potential allows an explicit construction of density functionals for the thermodynamics of nonequilibrium tunneling. I observe that it is possible to choose a detailed form of the adiabatic turn on such that it is compatible, even in a stringent mathematical sense, with both the requirement of LS collision DFT [64] and the present nonequilibrium thermodynamic description, appendix D. A robust, universally applicable, linking of the LS collision DFT with the nonequilibrium thermodynamics also requires an assumption of a V -representability¹⁹, i.e., that for every nonequilibrium electron density there exists an external potential for which the solution density matrix produces that density²⁰.

A solution nonequilibrium density matrix corresponding to a given density $n'(\mathbf{r}, t)$ can be viewed as a general density functional

$$\hat{\rho}_{n'}(t) = \hat{\rho}[n'(\mathbf{r}, t)] \equiv \hat{\rho}_{\text{col}, V' \leftarrow n'}(t). \quad (151)$$

Below I focus the discussion on steady-state transport in a time-independent scattering potential.

¹⁹For traditional time-dependent DFT calculations, where one can assume a finite extension of the system and hence system-specific potential, there exists a proof of uniqueness of density, see [162].

²⁰It is possible, but not clear, that the proof of the regular time-dependent DFT V -representability [162] also extends to transport calculations based on infinite-system time-dependent DFT [61, 161], to the LS collision DFT [64] formulation, and thus to the here-presented construction of a rigorous GCE thermodynamic DFT. However, the support of the system-specific SP potential term can in any case be made much larger than the extent of the actual laboratory and much larger than any four-probe measurement setup. I therefore here follow a common practice and simply assume that there exists at least an approximative V -representability.

The formally exact description of the overall dynamics in nonequilibrium tunneling also requires the introduction of a number of other density functionals²¹

$$F[n] = \frac{\text{Tr}\{\hat{\rho}_n[K + W + (1/\beta) \ln(\hat{\rho}_n/\text{Tr}\{\hat{\rho}_n\})]\}}{\text{Tr}\{\hat{\rho}_n\}}, \quad (152)$$

$$Y_V[n] \equiv Y_{\text{LS}}[n] = \frac{\text{Tr}\{\hat{\rho}_n \hat{Y}_V\}}{\text{Tr}\{\hat{\rho}_n\}}. \quad (153)$$

Here, \hat{Y}_V denotes the steady-state operator for the Gibbs free energy. The variational character of the thermodynamic potential can then be expressed

$$\Omega_V[n] = V[n] + F[n] - Y_V[n], \quad (154)$$

$$\begin{aligned} \frac{\partial \Omega_V[n]}{\partial n} &= \frac{\partial \Omega_V^{(0)}[n]}{\partial n} + \frac{\partial}{\partial n}[\Omega_V[n] - \Omega_V^{(0)}[n]] \\ &= 0. \end{aligned} \quad (155)$$

The correction to the noninteracting contribution in (155) is formally just a term which reflects an (effective-potential-type) extension to the SP dynamics discussed in section 7. However, equation (155) is not directly useful for a DFT formulation of efficient calculations of nonequilibrium GCE thermodynamics. As the subscript ‘ V ’ emphasizes, this is a formulation which would still require us to succeed with a complicated explicit construction [22, 23, 25] of the Gibbs free energy operator \hat{Y}_V that is specific for V and enters (153). Explicit solutions for \hat{Y}_V are possible [22, 23, 25–27] for special interacting-transport cases and reveal exciting details of interacting nonequilibrium dynamics. However, an approach based on (155) does not appear directly viable for setting up efficient SP calculations within a nonequilibrium thermodynamic DFT. Fortunately, there exists a work around.

8.2. Relation to standard ballistic-transport codes

The goal is frozen-nuclei calculations of the electron density (and of transmission and thermodynamic properties) in nonequilibrium tunneling within a generalization of the DBT framework [118–120, 122]. I consider only steady-state transport in a time-independent scattering potential and I introduce both a system-specific potential energy and (mean-field Coulomb) Hartree interaction terms

$$V[n] = \int d\mathbf{r} v_{\text{sc}}(\mathbf{r}) n(\mathbf{r}), \quad (156)$$

$$\Phi_{\text{H}}[n] = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (157)$$

Both are here expressed formally as density functionals.

Of central importance for the usefulness of the DBT method is undoubtedly the emphasis on using a density functional expression to approximate the effects of the many-body interaction. The DBT chooses to approximate these by using the exchange–correlation functional term

²¹Here and below I do not express the LS foundation in subscripts because I instead seek to emphasize the link to the density, namely via the specification $n \rightarrow V \rightarrow Y_V$, and thus, eventually, to the effective SP scattering potential V_{eff} .

(identified by ‘GS’) of the ground-state DFT, that is, approximations to the universal functional for equilibrium systems,

$$E_{xc}[n] = G_{GS}[n] - G_{GS}^{(0)}[n], \quad (158)$$

$$G_{GS}[n] = \langle \Psi_0 | K + W | \Psi_0 \rangle - \Phi_H[n], \quad (159)$$

$$G_{GS}^{(0)}[n] = \langle \Psi_0^{(0)} | K | \Psi_0^{(0)} \rangle \quad (160)$$

specified as a difference between expectation values of the fully interacting ground state $|\Psi_0\rangle$ and the noninteracting ground state $|\Psi_0^{(0)}\rangle$. From these functionals the DBT constructs an effective scattering potential

$$v_{\text{DBT}}[n](\mathbf{r}) \equiv v_{\text{sc}}(\mathbf{r}) + \frac{\delta \Phi_H}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}}{\delta n(\mathbf{r})}. \quad (161)$$

The fact that solutions of the DBT dynamics are expressed in terms of SP LS solutions ensures that the DBT method (for electron-density calculations) is inherently consistent, automatically satisfying conservation laws (for any given density functional choice). The DBT method incorporates the essential Gibbs free energy effects as it is consistent with the charge adjustments stipulated by using the Friedel sum rule on dynamics in the effective potential (161). In effect, the DBT method thus consists not only of constructing an effective potential $v_{\text{DBT}}[n]$ but also, implicitly, of constructing and using the associated SP Gibbs free energy operator,

$$\hat{Y}_{\text{DBT}}(\mathbf{r}) \equiv \sum_{\lambda_P} \mu_P (\hat{\psi}_{\text{DBT},\lambda_P}^{(0)})^\dagger \hat{\psi}_{\text{DBT},\lambda_P}^{(0)}, \quad (162)$$

from SP creation operators $(\hat{\psi}_{\text{DBT},\lambda_P}^{(0)})^\dagger$ for the set of DBT SP LS solution states.

A determination of the Gibbs free energy operator (and Gibbs free energy effects) is essentially already available at the DBT level. This opportunity exists because the DBT codes emphasize efficient calculations of the SP scattering states.

8.3. Universal functionals and formally exact single-particle descriptions

While the grand thermodynamical potential functional (154) contains a non-universal component (beyond $V[n]$), it is still possible to achieve an effective single-particle formulation in terms of universal density functionals. The development of a formally exact SP formulation shows that it contains the DBT method [118–120] as a lowest-order approximation (for frozen coordinates).

I observe that since the scattering potential is a functional of the density, equation (156), it follows that the LS operator solution can also be expressed as a density functional

$$\hat{\psi}_{\text{LS},\lambda_P}^\dagger[n] = \frac{i\eta}{\epsilon_{\lambda_P} + \mathcal{L}_{H_V \leftarrow n} + i\eta} c_{\lambda_P}^\dagger. \quad (163)$$

From this functional form of the many-body LS operator solution, it is possible to obtain density derivatives of the variational thermodynamic grand potential. I define

$$\hat{Y}_n = \sum_i \mu_i \hat{\psi}_{\text{LS},\lambda_P}^\dagger[n] \hat{\psi}_{\text{LS},\lambda_P}[n], \quad (164)$$

$$Y[n] = \frac{\text{Tr}\{\hat{\rho}_n \hat{Y}_n\}}{\text{Tr}\{\hat{\rho}_n\}}, \quad (165)$$

$$Y'[n] = \frac{\text{Tr}\{\hat{\rho}_n (\partial \hat{Y}_n / \partial n)\}}{\text{Tr}\{\hat{\rho}_n\}}. \quad (166)$$

I note that

$$\frac{\partial}{\partial n} Y_V[n] = \frac{\partial}{\partial n} Y[n] - Y'[n] \quad (167)$$

expresses the derivative of the Gibbs free energy in terms of universal functionals.

I seek an SP formulation where solving for fictitious SP scattering wavefunctions $\psi_{\text{eff},\lambda_P}(\mathbf{r})$ (moving in some effective scattering potential V_{eff}) constitutes a complete specification of both the electron density and the thermodynamic potential Ω_V . The individual SP scattering state is an SP LS solution which emerges from an H_d eigenstate λ_P (of energy ϵ_{λ_P}). Assuming a suitable normalization of such solutions leads to a simple determination of the electron-density variation,

$$n(\mathbf{r}) = \sum_{P,\lambda_P} |\psi_{\text{eff},\lambda_P}(\mathbf{r})|^2 \langle \hat{n}_{\lambda_P} \rangle_{\hat{\rho}_n}, \quad (168)$$

where $\langle \hat{n}_{\lambda_P} \rangle_{\hat{\rho}_n}$ is the level-occupation expectation value evaluated from $\hat{\rho}_n$. To provide a rigorous SP formulation from universal functionals I introduce a set of (generalized) exchange–correlation energy terms

$$F_{xc}[n] = F[n] - F^{(0)}[n], \quad (169)$$

$$Y_{xc}[n] = Y[n] - Y^{(0)}[n], \quad (170)$$

$$Y'_{xc}[n] = Y'[n] - Y'^{(0)}[n]. \quad (171)$$

Here, as before, superscripts ‘(0)’ identify functional values evaluated at $W = 0$. It follows that the fictitious dynamics is uniquely specified by an effective equation of motion

$$\begin{aligned} \frac{\partial \Omega_V^{(0)}}{\partial \psi_{\text{eff},\lambda_P}^*(\mathbf{r})} &= - \frac{\partial [\Omega_V - \Omega_V^{(0)}]}{\partial n} \psi_{\text{eff},\lambda_P}(\mathbf{r}) \\ &= - \left(\frac{\delta F_{xc}[n]}{\delta n(\mathbf{r})} - \frac{\delta Y_{xc}[n]}{\delta n(\mathbf{r})} + Y'_{xc}[n] \right) \psi_{\text{eff},\lambda_P}(\mathbf{r}). \end{aligned} \quad (172)$$

Since we have assumed a suitable normalization, the equation of motion for an occupied SP LS solution wavefunction can be reformulated,

$$\begin{aligned} \langle \mathbf{r} | (H_V^{(0)} - \hat{Y}_V^{(0)}) | \psi_{\text{eff},\lambda_P} \rangle \\ + \left(\frac{\delta F_{xc}[n]}{\delta n(\mathbf{r})} + Y'_{xc}[n] - \frac{\delta Y_{xc}[n]}{\delta n(\mathbf{r})} \right) \langle \mathbf{r} | \psi_{\text{eff},\lambda_P} \rangle \\ = C[\psi_{\text{eff},\lambda_P}](\epsilon_{\lambda_P} - \mu_P) \langle \mathbf{r} | \psi_{\text{eff},\lambda_P} \rangle. \end{aligned} \quad (174)$$

The real-valued functional $Y'_{xc}[n]$ can be viewed either as a constant potential shift or as a shift in the eigenvalue ϵ_{λ_P} , for example, as expected when an infinite scattering potential causes a change in band structure [133, 134].

The SP LS scattering-wave solution (for dynamics in an effective SP potential V_{eff} that gives rise to the SP Gibbs free energy operator $\hat{Y}_{V_{\text{eff}}}$) is

$$\langle \mathbf{r} | (H_{V_{\text{eff}}}^{(0)} - \hat{Y}_{V_{\text{eff}}}^{(0)}) | \psi_{\text{eff},\lambda_P} \rangle = (\epsilon_{\lambda_P} - \mu_i) \langle \mathbf{r} | \psi_{\text{eff},\lambda_P} \rangle. \quad (175)$$

Given an assumption of V -representability, it follows that the terms of the fictitious SP formulation (175) and the variational evaluation (174) must coincide. This provides a framework to identify the uniquely defined effective SP potential

$$V_{\text{eff}}[n] \equiv \int d\mathbf{r} v_{\text{eff}}[n](\mathbf{r})n(\mathbf{r}). \quad (176)$$

At the same time, and unlike in ground-state DFT and in DBT, it is not so that a comparison of the dynamics specified by the variational principle leads directly to an explicit determination of a new effective potential,

$$V_{\text{eff}}[n] \neq V[n] + \frac{\delta}{\delta n} F_{\text{xc}}[n]. \quad (177)$$

To search for an effective SP potential for the description of many-body interaction effects in nonequilibrium tunneling we must instead require an implicit approach with concerted adjustments of both the potential form and the associated Gibbs free energy term. Future works will explore approaches for simplifying this implicit search for the effective SP scattering potential (going beyond the DBT approach).

Nevertheless, we are able to now discuss the nature of the DBT method for calculations of electron density as a lowest-order approximation to the above-discussed, exact GCE thermodynamic DFT. It is clear that the DBT method is consistent: it is built from SP LS scattering states and it follows that the description (in itself) is compatible with the Friedel sum rule. The DBT method captures Gibbs free energy effects (to the extent that these arise in the DBT choice of the effective potential (161)) through the implicit construction of the quadratic operator \hat{Y}_{VDBT} , equation (162). Within the DBT calculation method one can also define the DBT solution density matrix as a density functional $\hat{\rho}_n^{\text{DBT}}$ and, in turn a density functional for the DBT approximation for the Gibbs free energy in an actual potential V ,

$$Y_V^{\text{DBT}}[n] = \frac{\text{Tr}\{\hat{\rho}_n^{\text{DBT}} \hat{Y}_{\text{VDBT}}\}}{\text{Tr}\{\hat{\rho}_n^{\text{DBT}}\}}. \quad (178)$$

The DBT method does constitute an approximation in that it does not express the thermodynamics in terms of the actual functionals $F_{\text{xc}}[n]$, $Y_{\text{xc}}[n]$ and $Y'_{\text{xc}}[n]$. A systematic improvement of the DBT method can be made by also consistently including the nonequilibrium many-body scattering effects which are expressed in the functional-derivative difference

$$\begin{aligned} & \frac{\delta}{\delta n(\mathbf{r})} (F_{\text{xc}}[n] - E_{\text{xc}}[n] - \Phi_{\text{H}}[n]) \\ & - \frac{\delta}{\delta n(\mathbf{r})} (Y_{\text{xc}}[n] - Y_V^{\text{DBT}}[n] + Y_V^{(0)}[n]) + Y'_{\text{xc}}[n] \neq 0. \end{aligned} \quad (179)$$

8.4. Nonequilibrium thermodynamics in interacting tunneling

With the universal functionals, the SP formulation and the generalized Hellmann–Feynman, it is possible to formally set up rigorous DFT calculations of the exact steady-state thermodynamic variation and of the associated conservative,

adiabatic forces. The nonequilibrium Green function or the phase-shift formulations (section 2.2) are viable frameworks for DFT SP studies of fully interacting nonequilibrium tunneling.

Such formal DFT calculations provide a determination of the change in the thermodynamic grand potential value but only given relative to the (fixed, infinite) value which characterizes the initially disconnected system H_{d} . This is natural as the open model systems are extensive (infinite) and no other determination would make sense. I also note that the disconnected equilibria system H_{d} might well be given by a ground-state DFT calculation of those manifestly equilibrium $t \rightarrow -\infty$ subsystems. This implies that it is possible to obtain a starting point which is exactly characterized (through the Kohn–Sham eigenstates and eigenvalues). It also implies that one can have a starting point where the expected density changes (and hence the changes in the effective scattering potential) will remain essentially confined to the central tunneling region. While the transmission, in principle, implies that the density changes extend to infinity, this density component will not generally affect the resulting effective potential far from the central tunneling region. This is an observation which has been explicitly tested in a typical DBT study [120].

Computations of the thermodynamic grand potential based on the Green function formulation [148] (appendix A) can build on significant experience. Formal scattering theory evaluations, based on a rapidly convergent expansion in the T -matrix behavior, were emphasized already in the early DFT history. The approach was, for example, used in studies of the van der Waals binding and kinetic energy repulsion of noble gas atoms on a metal surface [149, 150]²². This type of scattering-system calculation is also actively pursued for nonequilibrium systems within the ReNSQM framework and calculations are available even for the more complex interacting nonequilibrium tunneling problems [22–27]. In addition, the phase-shift analysis (appendix B) suggests that DBT computations can provide a shortcut, at least in simpler cases where it is possible to complete a S -matrix eigenstate decomposition.

9. Discussion

The rigorously demonstrated existence of an exact, variational thermodynamic grand potential is important in itself as it leads to an exact SP computational framework (results (a) through (d)) of, for example, the electron density. At that stage, the theory constitutes an alternative to adaptations [61, 161] of time-dependent DFT [53] to a GCE modeling framework of tunneling although the functionals are different, constructed from a thermodynamic rather than an action principle.

The fact that the nonequilibrium thermodynamic grand potential is even extremal allows it to deliver additional conclusions (results (e) through (j)); it is relevant to seek a rigorous computation also of the variational quantity $\Delta\Omega_{\text{LS}}$ itself.

²²For a recent summary and comparison with van der Waals density functional calculations, please see [163].

9.1. Thermodynamic versus electrostatic forces

It is interesting that the here-derived exact thermodynamic forces (4) formally and generally differ,

$$\mathbf{F}_{\mathbf{R}_i}^{\text{es,NEQ}} \neq \mathbf{F}_{\text{LS},\mathbf{R}_i}^{\text{GCE}}, \quad (180)$$

from the often-used GCE electrostatic forces, (6). The electrostatic-force expressions (6) are specified by frozen-nuclei calculations of the nonequilibrium electron-density variation and they are often—but need not be—used to thus predict nonequilibrium atomic relaxations from DBT or nonequilibrium quantum statistical mechanics calculations [97–100, 103, 104, 106, 107, 110, 139, 140].

I observe that the use of electrostatic forces lacks a formal foundation beyond (equilibrium and) linear response. Like [97], I point out that the Ehrenfest theorem [141] cannot be used for a conclusive determination of forces by electrons on the nuclei for infinite open systems. One can succeed with an Ehrenfest-based force evaluation (and derive electrostatic forces),

$$i \frac{d}{dt} \left\langle \frac{\partial}{\partial \mathbf{R}_i} \right\rangle \Big|_{\text{GS or finite}} = \left\langle \frac{\partial H}{\partial \mathbf{R}_i} \right\rangle \Big|_{\text{GS or finite}}, \quad (181)$$

of course, for finite systems [141] or in a standard ground-state DFT formulation²³. A force evaluation based directly on Ehrenfest theorem is also available for studies using traditional, finite-extension canonical-ensemble time-dependent DFT [165, 166] and when the nonequilibrium transport problem is recast as a finite (essentially closed) problem [62, 63], i.e., when a time-dependent field causes induction (balanced by a coupling to a phonon bath) in a horse-shoe setup. However, for the standard open-boundary modeling of tunneling an analysis in terms of GCE thermodynamics remains essential.

An attempt at a direct evaluation of the Ehrenfest theorem is indeterminate in a GCE description of tunneling. This is because such systems, by nature, must have infinite extension to avoid carrier depletion. Ehrenfest evaluation of forces (for SP dynamics) rests on using the Green theorem,

$$\int_V (u \Delta v - v \Delta u) \, d\mathbf{r} = \int_S (u \nabla v - v \nabla u) \cdot d\boldsymbol{\tau}, \quad (182)$$

and on using an assumed cancellation of the surface terms (in ‘S’) at infinity [141]. There is no argument directly available for a cancellation for scattering states. In fact, inclusion of surface terms is essential for both the formal SP collision formulation [124], for a consistent nonequilibrium Green function evaluation of noninteracting tunneling transport²⁴ [41], and for an LS collision description

of an open many-body interaction problem [123, 167]. The evaluation must be pursued in the context of a Wronskian [144] formulation, i.e., with adherence to the flux conservation that formal scattering theory automatically provides [138].

This paper shows (appendix A) that the exact thermodynamic forces (5) reduce to the electrostatic force definition (6) when the electron distribution can be entirely described from the full density of states. I note that this condition is not generally satisfied outside equilibrium. Before proceeding, I also emphasize that the here-presented formal and exact QKA recasts rigorously demonstrate that the steady-state thermodynamic forces for adiabatic transformation can never reduce to the nonconservative electrostatic forces discussed and explored, for example, in [106, 107].

Many existing descriptions of tunneling forces start with the definition (6) and the assumption that since electrostatic forces are applicable in equilibrium and in linear response [87, 98] they should also hold under general nonequilibrium conditions. The assumption of the validity of electrostatic forces (6) enters, for example, as expressed by a choice of Lagrangian [104], or when motivation is sought from the Ehrenfest theorem [141] followed by an Ehrenfest approximation, i.e., a separation of slow nuclei and fast electron dynamics [97, 99, 100].

There are ongoing discussions of run-away and possible water-wheel nucleus dynamic effects²⁵ [103, 104, 106, 107, 110] and of an inherent nonconservative nature [87, 106, 107] of such electrostatic forces. These discussions have recently been supplemented by works which also include a coupling to a phonon bath [109, 110]. Typically, it is the electron behavior expressed by (6) which is seen as the source for a possible structural instability in tunneling systems. Several papers (for example, [110]) state that the nonconservative behavior expresses a nonadiabatic property (a view that is consistent with the here-presented finding that the exact steady-state thermodynamic forces must be explicitly conservative). Inclusion of phonons tends to stabilize the dynamics [109, 110]. The papers on nonconservative electrostatic forces discuss an effect beyond Joule heating, an effect which should arise also in the absence of a possible current-induced coupling to vibrations. The latter effect is clearly also important, for example, as has very recently been illustrated [109] in a study of a current-induced limit-cycle behavior produced when focusing the many-body interaction to an electron–vibrational coupling. Overall, this development, a finding of a nonconservative character in the forces which are widely used for implementing nonequilibrium relaxations,

²³ Ehrenfest theorem can be used for an equilibrium canonical-ensemble system by first assuming an infinite repetition and by then employing a periodic-cell Green theorem, [164].

²⁴ The role of the Green-theorem surface terms (in a consistent determination of noninteracting Green functions for tunneling [37]) is not always expressed but they are nevertheless essential [41] (until one includes actual many-body scattering and associated dephasing effects everywhere). In the nonequilibrium Green function descriptions, we traditionally seek to separate out the single-particle terms (here denoted δKV) and many-body terms

(described by a self-energy σ). In the absence of many-body interactions (or dephasing) in the leads, the Green-theorem surface terms force us to work with $g_{<} = [1 + g_r(\delta KV + \sigma_r)]g_{<}^d [(\delta KV + \sigma_a)g_a + 1] + g_r\sigma_{<}g_a$, not just the last term (that vanishes when $\sigma = 0$).

²⁵ Including an electron–phonon coupling will obviously provide a modeling of Joule heating of the lattice and, hence, of a friction mechanism. However, it also opens up for both possible topological effects [110] and frequency-selective, current-induced spontaneous emission as well as stimulated transitions, for example, as discussed in [102].

accentuates the need for discussing which forces are best suited to describing working nonequilibrium devices.

This paper concentrates the discussion of forces and relaxations on the strictly adiabatic behavior, arising when there is an infinite ratio of the ion to electron masses. For this discussion I find that the exact thermodynamic forces are not only variational and explicitly conservative but also express an inherent adiabatic nature (always propelling the system to a state without any thermodynamic excitation). I find that the thermodynamic forces are suited for use in a nonequilibrium Born–Oppenheimer approximation.

It is, of course, clear that additional nonconservative forces, like wind forces, will also apply when one cannot ignore the mass and momentum of the electron in the thermodynamic analysis. Understanding the nature of nonadiabatic forces is also an important problem which, however, lies beyond the scope of this paper.

9.2. Relation to equilibrium thermodynamics

The demonstration of the variational character (appendix C) is essentially identical to Mermin’s original analysis [52] in his formulation of an equilibrium thermodynamic DFT. However, one difference deserves a separate discussion: the emerging (rather than fixed) expression for the nonequilibrium Gibbs free energy operator $\hat{Y}_{\text{col}}(t)$ does not seem to provide any *reductio ad absurdum* argument. Rather, changes in the SP collision potential term V_{col} will make themselves felt both in the Hamiltonian and in the Gibbs free energy operator.

Nevertheless, the present nonequilibrium thermodynamic account is developed in the continuum Caroli partition scheme [32, 33] that was also used in the formulation [64] of an LS collision DFT. Rather than a traditional *reductio ad absurdum* argument [52], it is here a time-dependent DFT-type of argument (from the appendix of [64] or from [161]) that underpins a DFT SP formulation. This analysis ensures that one can treat both the nonequilibrium thermodynamic quantities and associated nonequilibrium density matrix solutions through universal electron-density functionals.

9.3. Refining the density functional description

I note that many-body interactions in nonequilibrium tunneling are known to cause changes in the statistical distribution among many-body eigenstates [21, 22, 24, 25, 27] in tunneling. The magnitude and complexity of such changes significantly exceed those arising in equilibrium cases because the Fermi-liquid behavior degrades and genuine inelastic processes will proceed [37, 41, 42, 129].

The Friedel sum rule is, of course, also of central importance in correct calculations of such many-body interactions [137, 143]. In addition, it is in nonequilibrium tunneling a much more complex task to determine which possible many-body states represent the lower- or higher-lying many-body configurations of the emerging distribution [21]. A full, exact GCE thermodynamical account is essential to decide which many-body configurations must be excluded in an implementation of an adiabatic transformation of nuclei positions.

10. Summary and conclusion

To derive a rigorous description of GCE thermodynamics in interacting nonequilibrium tunneling, this paper recasts the full QKA [15] of electron dynamics. It identifies a variational thermodynamic grand potential in a theory that is closely related to the exact steady-state ReNQSM [21] and to Mermin’s analysis of equilibrium GCE thermodynamics [52]. In part, this formal result is made possible by definition of an operator for the nonequilibrium Gibbs free energy under general nonequilibrium tunneling conditions. The paper furthermore notes the existence of a uniqueness of density proof (from the closely related LS collision DFT [64]) and uses that proof, and the extremal nature of the nonequilibrium grand potential, to formulate rigorously an SP thermodynamic theory cast in terms of universal density functionals. The density functionals characterize the internal and Gibbs free energy variation. The paper establishes the widely used DBT formulation [118] as a lowest order yet consistent approximation to the here-presented nonequilibrium thermodynamic DFT.

A nonempirical theory of nonequilibrium tunneling must be able to reliably describe the structure of a tunneling system under the operating conditions and, in particular, to determine transport-induced morphology changes. This has been a challenge because in actual nonequilibrium quantum statistical mechanics calculations the focus is typically on the electron behavior. For the standard (open-boundary and thus infinite) model framework of tunneling, I observe that there is a need to include effects of the Gibbs free energy variation. For example, electron redistribution effects [21, 23, 25, 41, 42, 129] make it relevant to investigate and determine thermodynamic forces. The demonstration of a generalized Hellmann–Feynman theorem ensures a conservative nature of the thermodynamic forces.

This paper has thus taken a fundamentally different route from the standard force discussion and has avoided an indeterminate Ehrenfest-type force evaluation. This paper demonstrates that the here-defined exact thermodynamic forces are useful and will always implement (with sufficiently slow deformation) an adiabatic nature in relaxations. The thermodynamic forces are also based on a robust physics principle (entropy maximization) and are suited for use in a nonequilibrium Born–Oppenheimer approximation for interacting nonequilibrium tunneling.

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Appendix A. Noninteracting Green function analysis

The emitter ‘L’ and collector ‘R’ are initially described by states $|\phi_{\lambda,L/R}\rangle$ (of SP energy $\epsilon_{\lambda,L/R}$) but have no overlap with

each other or with states of the central region $|\phi_{\lambda,C}\rangle$. The initial (disconnected) system is described by retarded Green functions

$$\hat{g}_r^d(\omega) = \sum_{J=L/R/C} \hat{g}_r^{dJ}(\omega), \quad (\text{A.1})$$

$$\hat{g}_r^{dJ=L/R/C}(\omega) = \sum_{\lambda} \frac{|\phi_{\lambda,J}\rangle\langle\phi_{\lambda,J}|}{\omega - \epsilon_{\lambda,J} + i\eta}. \quad (\text{A.2})$$

From these one can determine the initial density of state as a trace

$$\mathcal{D}^d(\omega) = \sum_{J=L/C/R} \mathcal{D}^{dJ}(\omega), \quad (\text{A.3})$$

$$\mathcal{D}^{d,J=L/R/C}(\omega) = \frac{i}{\pi} [\hat{g}_r^{dJ}(\omega) - \hat{g}_a^{dJ}(\omega)], \quad (\text{A.4})$$

using the general analytic properties of the retarded and advanced Green functions, $\hat{g}_a(\omega) = \hat{g}_r^*(\omega)$. The density of state includes a factor of 2 for spin. A specification of the electron distribution or less-than Green function is given in section 7.3.

I provide below a formal nonequilibrium Green function (or equivalently an SP LS solution) framework for calculations and analysis in noninteracting GCE thermodynamics.

A.1. From noninteracting Green functions to nonequilibrium thermodynamics

For the emitter and collector we seek the partial or projected density of state changes (19) as well as the corresponding integrated changes (21). The integrated density of state changes (21) reflect the net effects of the infinitesimal level shifts ($\epsilon_{\lambda,p} \rightarrow \tilde{\epsilon}_{\lambda,p}$) that arise with the adiabatic turn on of the tunneling and which are reflected in the SP LS solutions [124, 134, 146]

$$|\psi_{\text{LS},\lambda,p=L/R}^{(0)}\rangle = [1 + \hat{g}_r^d(\tilde{\epsilon}_{\lambda,p})\hat{T}^{(0)}(\tilde{\epsilon}_{\lambda,p})]|\phi_{\lambda,p}\rangle. \quad (\text{A.5})$$

Here $\hat{T}^{(0)}$ denotes the T matrix of the connected (but noninteracting) system. In fact, the set of SP LS solution states, $\{|\psi_{\text{LS},\lambda,p=L/R}^{(0)}\rangle\}$, can be used to determine the full change in the density of state [149] as well as the lead-projected density of state changes, (19).

The full density of state change (in the connected but noninteracting system),

$$\Delta\mathcal{D}_{\text{tot}}(\omega) = \Delta\mathcal{D}_L(\omega) + \Delta\mathcal{D}_R(\omega) \quad (\text{A.6})$$

$$= \mathcal{D}^d(\omega) + \frac{i}{\pi} \text{Tr}\{\hat{g}_r^d(\omega)\hat{T}^{(0)}(\omega)\hat{g}_r^d(\omega)\}, \quad (\text{A.7})$$

reflects the full S - and T -matrix behavior (expressed in (7)). The Dyson equation [132] for the retarded Green function

$$\hat{g}_r^{(0)}(\omega) - \hat{g}_r^d(\omega) = \hat{g}_r^d(\omega)H_{1,V}\hat{g}_r^{(0)}(\omega) \quad (\text{A.8})$$

determines the energy levels $\epsilon_{\lambda,p}$, formally by solving for the poles of the scattering-state retarded Green function [134, (141) and (142)]. In turn, this formal scattering theory analysis

uniquely determines the tunneling-induced changes in the zero-temperature thermodynamic grand potential

$$\begin{aligned} \Delta\Omega_{\text{LS}} &= \sum_{P=L/R} \int_{-\infty}^{\mu_P} (\omega - \mu_P)\Delta\mathcal{D}_P(\omega) \\ &= - \sum_{P=L/R} \int_{-\infty}^{\mu_P} \Delta\mathcal{N}_P(\omega). \end{aligned} \quad (\text{A.9})$$

A.2. Grand canonical-ensemble thermodynamic study of Cu(111) adsorbates

The interactions of Cu(111) adsorbates provide a simple example of the role of the Gibbs free energy in a GCE thermodynamic study (section 2.3). This is a system where it is sufficient to consider adsorbate-induced s-wave scattering phase shifts [2, 126]. Here I provide some details on the thermodynamic behavior from the Green function calculations which underpin the results, for example, reported in [4, 147, 155]. The isotropic surface state has an approximative free-electron dispersion [168] given by the effective mass m_{eff} . At the same time, it is an example which requires formal scattering theory because the MSS scattering off, for example, an adatom must be described nonperturbatively [126] and the same therefore applies for the description of the MSS-mediated interaction [147].

I introduce an MSS Fermi energy ϵ_F to express the difference between the chemical potential μ_F and the bottom of the MSS state (in a zero-temperature analysis). The unperturbed two-dimensional dynamics is expressed in terms of the MSS retarded Green functions

$$g_r^{\text{MSS}}(d; \omega) = \frac{m_{\text{eff}}}{\pi\hbar} K_0(-iq_{\omega}r + i\eta). \quad (\text{A.10})$$

Here $\hbar\omega \equiv \hbar^2 q_{\omega}^2/2m_{\text{eff}}$ and K_0 denotes the two-dimensional zeroth-order Bessel function. Since the experimental and theoretical characterizations rest on an s-wave description of the adatom–MSS interaction, I also introduce the MSS T -matrix

$$T_{1s}(\omega) = \frac{i\hbar^2}{m_{\text{eff}}} [e^{i2\delta_0(\omega)} - 1] \quad (\text{A.11})$$

for multiple δ -function scattering [147]. This energy-dependent T -matrix is given by the s-wave phase shift

$$\delta_0(\omega) = \text{arccot}[\ln(\omega/\epsilon_F)/\pi + \cot(\delta_F)], \quad (\text{A.12})$$

which, in turn, is entirely specified by the experimentally observed Fermi level (s-wave) phase shift, $\delta_F \approx \pm\pi/2$.

The MSS-mediated interaction is given by evaluating the integrated change in the density of states, $\Delta\mathcal{D}_{\text{MSS},2s}^{\delta_F}(d; \omega)$, which arises when two adatoms approach from an infinite distance and to some finite separation d .

Since this is an equilibrium problem, one can use Lloyds' formula [156] to directly express the integrated changes in the density of state as the two s-wave scatterers approach from an infinite separation to some finite separation d ,

$$\Delta\mathcal{N}_{\text{MSS},2s}^{\delta_F}(d; \omega) = -2\text{Im} \ln\{1 - [T_0^{\delta_F}(\omega)g_r^{\text{MSS}}(\omega, d)]^2\}. \quad (\text{A.13})$$

Using also formal Fourier-transformation theory, for example, as formulated by Lighthill [158], it is straightforward to obtain an analytical evaluation in the limit of asymptotic adatom separation, $q_F d \gtrsim \pi$. In particular, it follows that the asymptotic internal energy variation is entirely dominated by [157]

$$\Delta N_{\text{MSS},2s}^{\delta_F}(d; \omega) \sim \left(\frac{2}{\pi}\right)^2 \text{Re} \left[\frac{e^{i2q_F d \sqrt{y}}}{q_F d \sqrt{y}} \times \frac{(\ln(y)/\pi + \cot(\delta_F) + i)^2}{[1 + (\ln(y)/\pi + \cot(\delta_F))^2]^2} \right]_{y=\omega/\epsilon_F}. \quad (\text{A.14})$$

The leading-order GCE variation in internal energy $U_{\text{LS}}^{\text{MSS},2s}(d; \delta_F)$ coincides exactly with the variation predicted for the Gibbs free energy, $Y_{\text{LS}}^{\text{MSS},2s}(d; \delta_F) = \mu_F \Delta N_{2s}(\epsilon_F; \delta_F)$. The asymptotic decay $1/d$ of either of the individual GCE interaction components differs from the $1/d^2$ decay form derived in a previous perturbative canonical-ensemble calculation [154] and from experimental observations [126].

The full GCE thermodynamic account, calculating the GCE thermodynamic grand potential for the MSS-mediated interaction interactions, has instead a cancellation of the $1/d$ terms and has a correct $1/d^2$ oscillatory decay as well as a phase in agreement with the experiments [126]. The analysis thus illustrates that including the Gibbs free energy variation is essential in formal scattering theory studies of the GCE thermodynamic behavior [147, 149, 150].

A.3. Thermodynamic versus electrostatic forces

Here I explore the consequences of an assumption ‘(A)’ that the electron distribution, i.e., $g_{<}^{(0)}(\mathbf{r}, \mathbf{r}, \omega)$, remains entirely specified by the changes in the full local density of state,

$$\mathcal{D}_{\text{tot}}(\mathbf{r}, \omega) \equiv -\frac{2}{\pi} \text{Im}(\mathbf{r}|\hat{g}_{\mathbf{r}}^{(0)}\omega|\mathbf{r}). \quad (\text{A.15})$$

For a discussion of electrostatic forces it is relevant to also inspect the variation in the corresponding integral

$$\mathcal{N}_{\text{tot}}(\mu') \equiv \int_{-\infty}^{\mu'} d\omega \int d\mathbf{r} \mathcal{D}_{\text{tot}}(\mathbf{r}, \omega). \quad (\text{A.16})$$

Assumption (A) applies in equilibrium [13]. When assumption (A) applies it allows an important simplification through a Lloyds’ formula [156] evaluation of the thermodynamic grand potential and causes the thermodynamic forces to reduce to electrostatic forces. I stress that assumption (A) is not expected to hold under nonequilibrium conditions and that there is no argument that an equivalence of thermodynamic and electrostatic forces holds in general.

Lloyds’ formula [156] is a succinct formulation of the full density of state changes

$$\Delta \mathcal{D}_{\text{tot}}(\omega) = -\frac{\partial}{\partial \omega} \frac{2}{\pi} \text{ImTr}\{\ln[1 - H_{1,V} g_{\mathbf{r}}^d(\omega)]\} \quad (\text{A.17})$$

arising, for example, with the adiabatic turn on of a tunneling term $H_1^{(0)}$. Lloyds’ formula rests on the simple observation that

$$-\frac{\partial}{\partial \omega} \hat{g}_{\mathbf{r}}(\omega) = \hat{g}_{\mathbf{r}}(\omega) \hat{g}_{\mathbf{r}}(\omega) \quad (\text{A.18})$$

and the possibility for using a cyclic permutation of operations when evaluating a full trace. Lloyds’ formula (A.17) leads directly to a compact evaluation of the integral of the full density of state changes $\Delta \mathcal{N}_{\text{tot}}(\omega)$.

Lloyds’ formula [156] provides significant advantages in calculation of forces when assumption (A) is applicable. Lloyds’ formula (A.17) can then be applied for an exact analysis of the additional changes produced in a noninteracting system by an infinitesimal adjustment, $H_{1,V} \rightarrow H_{1,V} + \delta V$. Here I take $\delta V = \int d\mathbf{r} \delta v(\mathbf{r}) \hat{n}(\mathbf{r})$; generalizations to other cases are straightforward. To lowest order in this infinitesimal additional perturbation δV one obtains from (A.17)

$$\delta \Delta \mathcal{N}_{\text{tot}}(\omega) = -\frac{1}{\pi} \text{Tr}\{\delta V [-2\text{Im}\hat{g}_{\mathbf{r}}^{(0)}(\omega)]\}. \quad (\text{A.19})$$

In an analysis of nonequilibrium conditions, I assume that $\mu_L > \mu_R$ and I formulate assumption (A) in terms of the contributions to the lead-specific less-than Green function contributions (section 2.2 and above). In general, it holds for the noninteracting nonequilibrium system that

$$\begin{aligned} \langle \mathbf{r}|\hat{g}_{<}^{(0)}\omega|\mathbf{r} \rangle &= \sum_{P=L/R} \langle \mathbf{r}|\hat{g}_{<,\mu_P}^{(0)P}\omega|\mathbf{r} \rangle \\ &= \pi \sum_{P=L/R} \mathcal{D}_P(\mathbf{r}, \omega) f_{\mu_P}(\omega), \end{aligned} \quad (\text{A.20})$$

$$\mathcal{D}_{\text{tot}}(\mathbf{r}, \omega) = \sum_P \mathcal{D}_P(\mathbf{r}, \omega), \quad (\text{A.21})$$

where $f_{\mu_P}(\omega)$ denotes the Fermi–Dirac distribution function. Assumption (A) can be expressed (for $P = L/R$) as

$$\langle \mathbf{r}|\hat{g}_{<,\mu_P}^{(0)P}\omega|\mathbf{r} \rangle = \kappa_P \pi f_{\mu_P}(\omega) \mathcal{D}_{\text{tot}}(\mathbf{r}, \omega), \quad (\text{A.22})$$

where $\kappa_{P=L/R}$ are would-be proportionality factors. Since the electron distribution for $\omega < \mu_R$ is no different than for a system in equilibrium, we must have $\kappa_L + \kappa_R = 1$ but this boundary condition is not used in the following analysis.

If assumption (A) holds, one can use Lloyds’ formula [156] in the following evaluation of the lead-specific contributions (for $P = L/R$) to the noninteracting thermodynamic grand potential:

$$\begin{aligned} \Omega_P &\rightarrow -2 \int_{-\infty}^{\mu_P} d\mu' \int d\mathbf{r} \int \frac{d\omega}{2\pi} \langle \mathbf{r}|\hat{g}_{<,\mu'}^{(0)P}\omega|\mathbf{r} \rangle \\ &= -2\kappa_P \int d\mu' \int d\mathbf{r} \int \frac{d\omega}{2\pi} \pi \mathcal{D}_{\text{tot}}(\mathbf{r}, \omega) f_{\mu'}(\omega) \\ &= -\kappa_P \int d\mu' \mathcal{N}_{\text{tot}}(\mu'). \end{aligned} \quad (\text{A.23})$$

Again, subject to (A) and thus the applicability of (A.22), it follows that infinitesimal changes in the potential (relevant for forces) correspond to changes in the lead-specific thermodynamic grand potential terms ($P = L/R$),

$$\delta \Omega_P \rightarrow \kappa_P \int_{-\infty}^{\mu_P} d\mu' \frac{1}{\pi} [-2\text{Im}\hat{g}_{\mathbf{r}}^{(0)}(\mathbf{r}, \mathbf{r}, \omega = \mu')] \delta v(\mathbf{r}) \quad (\text{A.24})$$

$$= 2 \int d\mathbf{r} \delta v(\mathbf{r}) \int \frac{d\omega}{2\pi} \langle \mathbf{r}|\hat{g}_{<,\mu_P}^{(0)P}(\omega)|\mathbf{r} \rangle. \quad (\text{A.25})$$

Assumption (A) implies for noninteracting-particle systems that the exact and explicitly conservative thermodynamic forces reduce to the widely used electrostatic forces

$$\begin{aligned} \frac{\partial \Omega_{\text{LS}}}{\partial \mathbf{R}_i} \cdot \delta \mathbf{R}_i &\rightarrow 2 \int d\mathbf{r} \delta v(\mathbf{r}) \int \frac{d\omega}{2\pi} \langle \mathbf{r} | \hat{g}_{<}^{(0)}(\omega) | \mathbf{r} \rangle \\ &= \left\langle \frac{\partial H^{(0)}}{\partial \mathbf{R}_i} \right\rangle_{\text{GCE}} \cdot \delta \mathbf{R}_i. \end{aligned} \quad (\text{A.26})$$

In summary, thermodynamic and electrostatic forces do coincide in equilibrium. There also exist arguments, summarized in [87], that electrostatic forces capture the adiabatic part of the force description in linear response. Under nonequilibrium conditions, however, assumption (A) is not expected to generally hold and there is then no argument that the thermodynamic and electrostatic forces should agree. This conclusion is corroborated by the phase-shift analysis in section B.

Appendix B. Phase-shift analysis of thermodynamics

To provide a phase-shift analysis of the thermodynamics in nonequilibrium tunneling it is advantageous to consider the state-specific contributions to the general formulation of the Friedel sum rule (7). I emphasize that the SP behavior expressed in the T -matrix reflects mutually independent dynamics and that the on-shell S -matrix is directly linked to the on-shell T -matrix,

$$S = 1 - 2\pi iT, \quad (\text{B.1})$$

$$T = \delta(\omega - H_V^0) T. \quad (\text{B.2})$$

In fact, the T - and S -matrices have identical eigenstates, here denoted $|j\rangle$.

The S -matrix (for particles at energy ω) has eigenvalues $\exp[2i\delta_j(\omega)]$ which, apart from the assumed spin degeneracy, reflect an isomorphic mapping to the set of initial states in the leads, namely the H_d SP eigenstates $|\lambda_{P=L/R}\rangle$. One can, as illustrated in figure 1, define a unitary transformation with matrix elements

$$\alpha_{j,\lambda_P} \equiv \langle j | \lambda_P \rangle, \quad (\text{B.3})$$

which expresses a representation change

$$S \longrightarrow \mathbf{d}_S = \alpha \cdot S \cdot \alpha^\dagger. \quad (\text{B.4})$$

This transformation diagonalizes the noninteracting S -matrix,

$$(\mathbf{d}_S)_{j,j'} = \delta_{j,j'} \exp[2i\delta_j(\omega)]. \quad (\text{B.5})$$

I observe in passing that the T -matrix is already by itself a powerful tool for approximating the dynamics even for the case of a nonperturbative interaction [147, 149]. One often obtains an excellent approximation by simply setting

$$\ln[S(\omega)] \approx -2\pi iT(\omega), \quad (\text{B.6})$$

an observation which suggests that we can use an S -matrix eigenstate analysis to assign an effective phase shift to each and every initial state $|\lambda_{P=L/R}\rangle$.

The argument for a state-specific evaluation can be made formal by considering a repeated application of the diagonalization (B.4) in every term of an expansion of the logarithm in (7),

$$\begin{aligned} \ln[S(\omega)] &= \alpha \ln[\mathbf{d}_S(\omega)] \alpha^\dagger \\ &= \alpha [2i\delta_j(\omega)] \alpha^\dagger. \end{aligned} \quad (\text{B.7})$$

Here $\alpha^\dagger |\lambda_P\rangle$ represents the state $|\lambda_P\rangle$ in the S -matrix eigenstate representation. An S -matrix eigenstate analysis will therefore directly give an evaluation of the state-specific density of state contribution

$$2i\pi [\delta(\omega - \tilde{\epsilon}_{\lambda_P}) - \delta(\omega - \epsilon_{\lambda_P})] \leftrightarrow \frac{\partial}{\partial \omega} \langle \lambda_P | \ln[S(\omega)] | \lambda_P \rangle \quad (\text{B.8})$$

$$= 2i \frac{\partial}{\partial \omega} \delta_{\lambda_P}(\omega). \quad (\text{B.9})$$

The latter expression is given in terms of an effective (state-projected) phase shift

$$\delta_{\lambda_P}(\omega) \equiv \sum_j \delta_j(\omega) |\langle j | \lambda_P \rangle|^2. \quad (\text{B.10})$$

It is interesting to link the above formal S -matrix description with the very general analysis of one-dimensional tunneling that is reported in [144]. That textbook analysis considers transmission in cases where the density of state and the group velocity are different in the two leads. That SP analysis is relevant for conditions which generally result with the application of a bias, for example, in modeling a heterostructure-based resonant tunneling diode [42, 46, 129]. For a propagating state ‘ u ’ (‘ v ’) originating from the far left (right) the transmission coefficients and reflection coefficients are expressed in polar notation

$$t_{u/v} = |t_{u/v}| \exp[i\Theta_t^{u/v}], \quad (\text{B.11})$$

$$r_{u/v} = |r_{u/v}| \exp[i\Theta_r^{u/v}]. \quad (\text{B.12})$$

The analysis of the finite-bias SP dynamics is based on evaluations of the Wronskian, i.e., with strict adherence to flux conservation, and identifies the general relations among the scattering phase shifts [144]

$$\Theta_t^u = \Theta_t^v, \quad (\text{B.13})$$

$$\Theta_r^u = \pi - \Theta_r^v + 2\Theta_t^u. \quad (\text{B.14})$$

Before proceeding, I observe that application of this textbook analysis formally requires a reinterpretation for use in the Caroli formulation. This is because the textbook analysis assumes the initial states to be propagating, i.e., not strictly limited to either of the leads as applies for $|\lambda_P\rangle$. However, the adaptation is straightforward and leads in a one-dimensional system to a simple explicit identification of an effective phase shift for the left-lead and right-lead states (at energy ω),

$$\delta_L^{\text{eff}}(\omega) = \Theta_r^u(\omega), \quad (\text{B.15})$$

$$\delta_R^{\text{eff}}(\omega) = \Theta_r^v(\omega). \quad (\text{B.16})$$

One can also define a total phase-shift derivative

$$\frac{\partial}{\partial \omega} \delta_{\text{tot}}^{\text{eff}}(\omega) \equiv \frac{\partial}{\partial \omega} \Theta_r^u(\omega) + \frac{\partial}{\partial \omega} \Theta_r^v(\omega) = 2 \frac{\partial}{\partial \omega} \Theta_r^u(\omega) \quad (\text{B.17})$$

that determines the full value of the integrated change in the density of state (115).

The above-described textbook analysis [144] of one-dimensional tunneling highlights the cause of differences between thermodynamic and electrostatic forces which arise under nonequilibrium conditions. Appendix A demonstrates that electrostatic forces result when (115) may be used to characterize the GCE thermodynamic change of an infinitesimal coordinate change. Section 2.2 explains that a full nonequilibrium characterization of the thermodynamic grand potential change in the limit of $\mu_L \gg \mu_R$ is instead completely specified by δ_L^{eff} . Different phase-shift variations characterize the two types of forces under nonequilibrium conditions. For example, when $\mu_L \gg \mu_R$ it holds that thermodynamic and electrostatic forces have different natures given by

$$F_{\mathbf{R}_i}^{\text{GCE}} \leftrightarrow \frac{\partial}{\partial \mathbf{R}_i} \delta_L^{\text{eff}}(\omega), \quad (\text{B.18})$$

$$F_{\mathbf{R}_i}^{\text{es,GCE}} \leftrightarrow \frac{\partial}{\partial \mathbf{R}_i} \delta_{\text{tot}}^{\text{eff}}(\omega), \quad (\text{B.19})$$

respectively. I stress that, for example in the one-dimensional model problem [144], there is no general relation between the transmission phase shift $\delta_{\text{tot}}^{\text{eff}}(\omega) = \Theta_r^u(\omega)$ and the reflection phase shift $\delta_L^{\text{eff}}(\omega) = \Theta_r^v(\omega)$ and that, consequently, there does not exist a general argument that the nonequilibrium electrostatic force agrees with the exact and explicitly conservative thermodynamic forces²⁶.

Appendix C. Mermin-type variational thermodynamics for nonequilibrium tunneling

This appendix summarizes the proof of the variational nature of the nonequilibrium thermodynamic grand potential and of the global-minimum property of the exact (solution) density matrix. The proof applies for time-independent or time-dependent interacting tunneling systems under nonequilibrium conditions defined as a collision problem, section 4. The argument is a straightforward generalization of Mermin's previous equilibrium analysis [52].

The first observation is that it is sufficient to prove the extremal property for any given time and hence I shall suppress all mention of subscripts 'col', 'sc' or 'LS' (as well as possible temporal arguments) in the following. A more compressed formulation of the extremal properties of the nonequilibrium thermodynamic grand potential, the nonequilibrium variational property, can thus be formulated as

$$\Omega[\hat{\rho}] > \Omega[\hat{\rho}_0] \equiv \Omega_0, \quad (\text{C.1})$$

²⁶The difference, $\Theta_r^u \neq \Theta_r^v$, is also important in a detailed analysis of tunneling times, cf reference [169].

where (for a Hermitian \hat{X}_0)

$$\hat{\rho}_0 \equiv \frac{e^{-\beta \hat{X}_0}}{\text{Tr}\{e^{-\beta \hat{X}_0}\}}, \quad (\text{C.2})$$

$$\Omega_0 \equiv -\frac{1}{\beta} \ln(\text{Tr}\{e^{-\beta \hat{X}_0}\}), \quad (\text{C.3})$$

$$\Omega[\hat{\rho}] \equiv \text{Tr}\{\hat{\rho}[X_0 + \beta^{-1} \ln \hat{\rho}]\}, \quad (\text{C.4})$$

and where trial nonequilibrium density matrices

$$\hat{\rho} = \frac{e^{-\beta \hat{X}}}{\text{Tr}\{e^{-\beta \hat{X}}\}} \quad (\text{C.5})$$

are given by any Hermitian operator \hat{X} .

As in the equilibrium theory, it is advantageous to also define a set of intermediate density matrices

$$\hat{\rho}_\lambda \equiv \frac{e^{-\beta \hat{X}_\lambda}}{\text{Tr}\{e^{-\beta \hat{X}_\lambda}\}}, \quad (\text{C.6})$$

$$\hat{X}_\lambda \equiv \hat{X}_0 + \lambda \Delta, \quad (\text{C.7})$$

where $\Delta \equiv -(1/\beta) \ln(\hat{\rho}) - \hat{X}_0$. This family of possible nonequilibrium density matrices (C.6) forms a line between $\hat{\rho}_0$ and $\hat{\rho}$ where each member formally represents (in the notation introduced in section 6) a solution of the thermodynamic grand potential

$$\begin{aligned} \Omega_{\hat{X}_\lambda} &\equiv \frac{\text{Tr}\{e^{-\beta \hat{X}_\lambda} (\hat{X}_\lambda + \beta^{-1} \ln \hat{\rho}_\lambda)\}}{\text{Tr}\{e^{-\beta \hat{X}_\lambda}\}} \\ &= -\frac{1}{\beta} \ln(\text{Tr}\{e^{-\beta \hat{X}_\lambda}\}) \neq \Omega[\hat{\rho}_\lambda]. \end{aligned} \quad (\text{C.8})$$

I note that, unlike in the equilibrium case, a separate argument (for example, V -representability) would be needed to conclude that any given member $\hat{\rho}_\lambda$ (of the line of density matrices) corresponds to an actual density matrix solution for a physical nonequilibrium tunneling system. However, such a representability assumption is not of any consequence for the proof and discussion of the extremal nature of the nonequilibrium thermodynamic theory. The essential observation is that all of the intermediate nonequilibrium density matrices (C.6) are still specified in the form given in (C.5).

The central step in the proof and argument is a demonstration of the variational property,

$$\frac{\partial}{\partial \lambda} \Omega_{\hat{X}_\lambda} = \text{Tr}\{\Delta \hat{\rho}_\lambda\}, \quad (\text{C.9})$$

that is, a compact formulation of the generalized Hellmann–Feynman theorem (105). Here the key observation is the general operator identity [52]

$$\frac{\partial}{\partial \lambda} e^{-\beta(\hat{X} + \lambda \Delta)} = -e^{-\beta(\hat{X} + \lambda \Delta)} \int_0^\beta d\beta' \Delta_\lambda(\beta'), \quad (\text{C.10})$$

$$\Delta_\lambda(\beta') \equiv e^{\beta'(\hat{X} + \lambda \Delta)} \Delta e^{-\beta'(\hat{X} + \lambda \Delta)}, \quad (\text{C.11})$$

which, of course, applies irrespective of the nature of the statistical ensemble, for nonequilibrium and equilibrium

conditions alike. Introducing also $\langle \hat{O} \rangle_\lambda \equiv \text{Tr}\{\hat{\rho}_\lambda \hat{O}\}$, one can thus formulate the parametric density matrix changes,

$$\frac{\partial}{\partial \lambda} \hat{\rho}_\lambda = - \int_0^\beta d\beta' \hat{\rho}_\lambda [\Delta_\lambda(\beta') - \langle \Delta \rangle_\lambda]. \quad (\text{C.12})$$

Mermin also makes the observation that a cyclic permutation of operators permits a significant simplification in the evaluation of expectation values, for example [52],

$$\langle \Delta_\lambda(\beta') \rangle_\lambda = \langle \Delta \rangle_\lambda. \quad (\text{C.13})$$

Inserting this result in (C.12) completes an explicit demonstration of the generalized Hellmann–Feynman result (C.9).

Finally, from (C.10) also follows a proof for the extremal nature of the thermodynamic grand potential. It proceeds by the reformulation of the potential derivative

$$\frac{\partial}{\partial \lambda} \Omega[\hat{\rho}_\lambda] = -\lambda \text{Tr} \left\{ \Delta \frac{\partial}{\partial \lambda} \hat{\rho}_\lambda \right\} \quad (\text{C.14})$$

$$= \lambda \int_0^\beta d\beta' |\langle \Delta_\lambda(\beta/2) - \langle \Delta \rangle_\lambda \rangle|^2. \quad (\text{C.15})$$

As in equilibrium thermodynamics, this result is sufficient to ensure that the difference $\Omega[\hat{\rho}] - \Omega[\hat{\rho}_0]$ is positive and cannot vanish except when $\hat{\rho} \equiv \hat{\rho}_0$.

In summary, the operator analysis of Mermin [52] is sufficient to ensure (not only for the equilibrium case but also for the present nonequilibrium thermodynamics) that the thermodynamic grand potential is both variational and extremal at the exact solution $\hat{\rho}_0$.

Appendix D. Linking the variational QKA of tunneling to LS collision DFT

The details of the continuum Caroli partition scheme, section 3, are designed to allow a combination of the LS collision DFT [64] with the present general nonequilibrium thermodynamic account. To accomplish that, it is necessary to also ensure that the choice of details in the adiabatic turn on (for the electron QKA) is made such that it permits the LS collision DFT proof of uniqueness of density. The underlying issue is purely technical, but for completeness I include here a mathematical analysis.

While [64] never explicitly stated this, the formal LS collision DFT proof of uniqueness of density does, in principle, require that the adiabatic turn on factor $a_\eta(t)$ vanishes not only at $t \rightarrow -\infty$, but also for all times $t < t_0$, where $t_0 \rightarrow -\infty$. In a strict mathematical sense, this is necessary because the LS collision DFT proof implicitly assumes one can work with a Taylor expansion in the temporal evolution. With the simple adiabatic turn on ($\tilde{a}_\eta(t) = \exp(\eta t)$) that we normally employ in the QKA, it follows that all Taylor-expansion coefficients of the temporal evolution vanish in the limit $t \rightarrow -\infty$. It is clear that just an extremely soft modification of the adiabatic turn on is required to ensure a rigorous mathematical description in the LS collision DFT analysis. It is also clear (because of the entropy flow) that such an extremely soft modification of the adiabatic turn on can have no consequence for the tunneling dynamics at relevant

times when a steady-state does emerge. The argument can be made formal.

To be specific I investigate an adiabatic turn on which (instead of the standard LS or QKA form, $\tilde{a}_\eta(t) = \exp(\eta t)$) is identically zero until some far away time $t_0 \rightarrow -\infty$. I assume that $a_\eta(t > t_0)$ is real, monotonically increasing, and satisfies $0 \leq a_\eta(t) \leq 1$, with a bounded derivative ($da_\eta/dt \leq \eta a_\eta(t)$). An explicit choice of slightly modified adiabatic turn on factors can be expressed as

$$a_\eta(t) = \exp(\eta t) b_\eta(t; t_0^\eta, t_1^\eta), \quad (\text{D.1})$$

where I have introduced a monotonically increasing positive function $b_\eta(t; t_0^\eta, t_1^\eta)$ with $b_\eta(t < t_0^\eta) \equiv 0$, $b_\eta(t > t_1^\eta) \equiv 1$ and $db_\eta(t)/dt \ll \eta$. I choose $t_1^\eta = -\eta^{-(\alpha+1)}$ (with $\alpha \rightarrow \infty$) and $t_0^\eta = t_1^\eta/\eta^2$. I note that this set of choices removes any possible $t = -\infty$ singularities in the LCS-DFT proof of uniqueness of density and I proceed to demonstrate that this modified adiabatic turn on still leaves all details of the formal LS solutions in the QKA unchanged (in the relevant limit $\eta \rightarrow 0^+$).

The important fact is that $da_\eta(t)/dt$ remains essentially specified by $\eta \exp(\eta t)$ since this factor, in turn, determines the denominator in the formal many-body LS solution (61). Focusing on the analysis in [134] I introduce

$$\hat{f}_\xi(t) \equiv e^{-i(E_\xi - H + i\eta)t}, \quad (\text{D.2})$$

$$\begin{aligned} \hat{F}_\xi(t) &\equiv \int_{-\infty}^t dt' \hat{f}_\xi(t') \\ &= \frac{i}{E_\xi - H + i\eta} e^{-i(E_\xi - H + i\eta)t}, \end{aligned} \quad (\text{D.3})$$

and note that the boundary condition, i.e., the original choice of adiabatic turn on $\exp(\eta t)$, enters the many-body LS solution through the formal evaluation [123, 134]

$$|\Psi_\xi^{(+)}\rangle = \eta \hat{F}_\xi(0) |\Phi_\xi\rangle. \quad (\text{D.4})$$

Using instead the present collision picture with slightly modified adiabatic turn on (D.1), the boundary condition instead enters the formal many-body solution through

$$\int_{-\infty}^0 dt' \hat{f}_\xi(t') b_\eta(t') = \hat{F}_\xi(t=0) - \hat{B}_\xi(\eta), \quad (\text{D.5})$$

$$\hat{B}_\xi(\eta) = \int_{t_0^\eta}^{t_1^\eta} dt' \hat{F}_\xi(t') \frac{db_\eta(t')}{dt'}, \quad (\text{D.6})$$

as obtained by partial integration. The resulting LS solution therefore has the form

$$|\bar{\Psi}_\xi^{(+)}\rangle = |\Psi_\xi^{(+)}\rangle - |\delta\Psi_\xi^{(+)}\rangle, \quad (\text{D.7})$$

$$|\delta\Psi_\xi^{(+)}\rangle = \eta \hat{B}_\xi(\eta) |\Phi_\xi\rangle. \quad (\text{D.8})$$

However, the relative normalization of the additional term in the modified many-body LS solution (D.8) is strongly bounded,

$$\| |\delta\bar{\Psi}_\xi^{(+)}\rangle \| \ll \eta \int_{t_0^\eta}^{t_1^\eta} dt' \| \eta e^{\eta t'} \hat{F}_\xi(0) |\Phi_\xi\rangle \|, \quad (\text{D.9})$$

$$< \mathcal{B}(\eta) \| |\Psi_\xi^{(+)}\rangle \|, \quad (\text{D.10})$$

by the (state-independent) evaluation

$$\mathcal{B}(\eta) \equiv \exp(\eta t_1^\eta) = \exp[-(1/\eta)^\alpha] \rightarrow 0. \quad (\text{D.11})$$

The choice $t_1^\eta = \eta^{-(\alpha+1)}$ with $\alpha \rightarrow \infty$ certainly ensures that $\mathcal{B}(\eta)$ and hence the modification (D.8) of the LS solution becomes irrelevant in the limit $\eta \rightarrow 0^+$.

In summary, I find that the LS collision DFT analysis [64] can be adapted to provide an independent proof for uniqueness of density while leaving the formal LS solutions of the many-body collision problems unchanged. This opens the way for a density functional formulation of the nonequilibrium thermodynamic quantities in a description which resembles the equilibrium case presented in [52].

Appendix E. Adiabatic changes in thermodynamic state functions

This appendix supplements the description of changes in the thermodynamic variation subject to the assumption of adiabatic transformations. That is, I derive formal expression for the changes in thermodynamic state functions with coordinate transformations, in essence, assuming that the evolving nonequilibrium density matrix is at all times (and for all evolving coordinates) given by the steady-state value. This analysis serves, for example, to detail the GCE breakdown in the traditional Hellmann–Feynman force evaluation.

The key observation is that the operator analysis of Mermin can be used to obtain the parametric derivatives of the unnormalized nonequilibrium solution density matrix, $\exp[-\beta(H - \hat{Y}_{\text{LS}})]$. For example, use of (C.10) and (C.13) directly leads to an evaluation of the entropy content,

$$\begin{aligned} \frac{\partial \bar{S}_{\text{LS}}}{\partial \mathbf{R}_i} &= -\beta^2 \left\langle [(H - \hat{Y}_{\text{LS}}) - (\bar{U}_{\text{LS}} - \bar{Y}_{\text{LS}})] \right. \\ &\quad \times \left. \frac{\partial(H - \hat{Y}_{\text{LS}})}{\partial \mathbf{R}_i} \right\rangle_{\hat{\rho}_{\text{LS}}}, \end{aligned} \quad (\text{E.1})$$

a form which is entirely specified by differences in internal energy and Gibbs free energy operators (and differences in their values).

There is a corresponding formal simplification in the evaluation of the expectation value of the Gibbs weighting factor,

$$\frac{\partial}{\partial \mathbf{R}_i} (\bar{U}_{\text{LS}} - \bar{Y}_{\text{LS}}) \equiv \frac{\partial}{\partial \mathbf{R}_i} \left(\bar{\Omega}_{\text{LS}} + \frac{1}{\beta} \bar{S}_{\text{LS}} \right). \quad (\text{E.2})$$

Using a cyclic permutation of operators in the trace yields

$$\begin{aligned} \frac{1}{\beta^2} \frac{\partial \bar{S}_{\text{LS}}}{\partial \mathbf{R}_i} &= (\bar{U}_{\text{LS}} - \bar{Y}_{\text{LS}}) \frac{\partial}{\partial \mathbf{R}_i} \bar{\Omega}_{\text{LS}} \\ &\quad - \frac{1}{2} \left\langle \frac{\partial}{\partial \mathbf{R}_i} (H - \hat{Y}_{\text{LS}})^2 \right\rangle_{\hat{\rho}_{\text{LS}}}, \end{aligned} \quad (\text{E.3})$$

and it follows that

$$\begin{aligned} \frac{\partial}{\partial \mathbf{R}_i} (\bar{U}_{\text{LS}} - \bar{Y}_{\text{LS}}) &= [1 + \beta(\bar{U}_{\text{LS}} - \bar{Y}_{\text{LS}})] \frac{\partial}{\partial \mathbf{R}_i} \bar{\Omega}_{\text{LS}} \\ &\quad - \frac{\beta}{2} \left\langle \frac{\partial(H - \hat{Y}_{\text{LS}})^2}{\partial \mathbf{R}_i} \right\rangle_{\hat{\rho}_{\text{LS}}}. \end{aligned} \quad (\text{E.4})$$

It is also possible to complete a formal evaluation of the derivatives of the total internal energy and Gibbs free energy (also when evaluated in isolation) thanks to the nature [21] of the Gibbs free energy or electron redistribution operator. In steady-state tunneling the Gibbs free energy must, of course, also be time independent. The time evolution is naturally formulated in terms of the Liouville operation

$$\mathcal{L}_H[\hat{Y}_{\text{LS}}] \equiv [\hat{Y}_{\text{LS}}, H] \propto \eta(\hat{Y}_{\text{LS}} - \hat{Y}_{\text{d}}) \rightarrow 0. \quad (\text{E.5})$$

The Gibbs free energy operator commutes with the interacting steady-state Hamiltonian $H \equiv H(t=0)$ in steady-state tunneling problems. As pointed out by Hershfield [21], the role of \hat{Y}_{LS} is to redistribute the electrons among the many-body eigenstates of H . Using the commutator result, $[H, \hat{Y}_{\text{LS}}] = 0$, together with Mermin's observation, (C.13), leads to the formal evaluations

$$\begin{aligned} \frac{\partial \bar{U}_{\text{LS}}}{\partial \mathbf{R}_i} &= \left\langle \frac{\partial H}{\partial \mathbf{R}_i} \right\rangle_{\rho_{\text{LS}}} + \beta \left\langle (H - \bar{U}_{\text{LS}}) \frac{\partial(H - \hat{Y}_{\text{LS}})}{\partial \mathbf{R}_i} \right\rangle_{\hat{\rho}_{\text{LS}}}, \quad (\text{E.6}) \\ \frac{\partial \bar{Y}_{\text{LS}}}{\partial \mathbf{R}_i} &= \left\langle \frac{\partial \hat{Y}_{\text{LS}}}{\partial \mathbf{R}_i} \right\rangle_{\rho_{\text{LS}}} + \beta \left\langle (\hat{Y}_{\text{LS}} - \bar{Y}_{\text{LS}}) \frac{\partial(H - \hat{Y}_{\text{LS}})}{\partial \mathbf{R}_i} \right\rangle_{\hat{\rho}_{\text{LS}}} \end{aligned} \quad (\text{E.7})$$

of the total internal energy and Gibbs free energy derivatives, respectively.

Finally I note that the reformulation of the derivative of the expectation value of the Gibbs weighting factor (E.4) can also be used to obtain an alternative expression of the here-defined thermodynamic forces,

$$\mathbf{F}_{\text{LS}, \mathbf{R}_i}^{\text{GCE}} = - \frac{\frac{\partial}{\partial \mathbf{R}_i} (H - \hat{Y}_{\text{LS}})_{\hat{\rho}_{\text{LS}}} + (\beta/2) \langle \frac{\partial}{\partial \mathbf{R}_i} (H - \hat{Y}_{\text{LS}})^2 \rangle_{\hat{\rho}_{\text{LS}}}}{1 + \beta(\bar{U}_{\text{LS}} - \bar{Y}_{\text{LS}})}. \quad (\text{E.8})$$

References

- [1] Bartels L 2010 *Nature Chem.* **2** 87
- [2] Han P and Weiss P S 2011 *Surf. Sci. Rep.* **67** 19
- [3] For examples of nonempirical studies of molecular-overlayer interaction problems, please see, e.g., Sony P, Puschnig P, Nabok D and Ambrosch-Draxl C 2007 *Phys. Rev. Lett.* **99** 176401
- Johnston K, Kleis J, Lundqvist B I and Nieminen R M 2008 *Phys. Rev. B* **77** 121404
- Toyoda K, Nakano Y, Hamada I, Lee K, Yanagisawa S and Morikawa Y 2009 *Surf. Sci.* **603** 2912
- Moses P G, Mortensen J J, Lundqvist B I and Nørskov J K 2009 *J. Chem. Phys.* **130** 104709
- Villagomez C J, Guillermet O, Goudeau S, Ample F, Xu H, Coudret C, Bouju X, Zambelli T and Gauthier S 2010 *J. Chem. Phys.* **132** 074705
- Zoppi L, Garcia A and Baldrige K K 2010 *J. Phys. Chem.* **114** 8864
- Lee K, Morikawa Y and Langreth D C 2010 *Phys. Rev. B* **82** 155461
- Ruuska H, Arola E, Kortelainen T, Rantala T T, Tapio T, Kannus K and Valkealahti S 2011 *J. Chem. Phys.* **134** 134904
- Klimes J, Bowler D R and Michaelides A 2011 *Phys. Rev. B* **83** 195131

- [4] Berland K, Einstein T L and Hyldgaard P 2009 *Phys. Rev. B* **80** 155431
- [5] Wyrick J, Kim D-H, Sun D, Cheng Z, Lu W, Zhu Y, Berland K, Kim Y S, Rotenberg E, Luo M, Hyldgaard P, Einstein T L and Bartels L 2011 *Nano Lett.* **11** 2944
- [6] Nykapanchuk D *et al* 2008 *Nature* **451** 549
Park S Y *et al* 2008 *Nature* **451** 553
- [7] For example, Gellman S H 1997 *Chem. Rev.* **97** 1231
Edmonson P J *et al* 2008 *Int. J. Mod. Sci.* **9** 154
- [8] For example, Rattner M A and Nitzan A 2003 *Science* **300** 1384
Pan S, Fu Q, Huang T, Zhao A, Wang B, Yang J and Hou J 2009 *Proc. Natl Acad. Sci. USA* **8** 15259
- [9] For example, Chen J, Reed M A, Rawlett A M and Tour J M 1999 *Science* **286** 1550
- [10] Bergmann P G and Lebowitz J L 1955 *Phys. Rev.* **99** 578
Lebowitz J L and Bergmann P G 1957 *Ann. Phys.* **1** 1
- [11] Fano U 1957 *Rev. Mod. Phys.* **29** 74
- [12] Baym G and Kadanoff L P 1961 *Phys. Rev.* **124** 287
Baym G 1962 *Phys. Rev.* **127** 1391
- [13] Kadanoff L P and Baym G 1962 *Quantum Statistical Mechanics* (New York: Benjamin)
- [14] Keldysh L V 1964 *Zh. Eksp. Teor. Fiz.* **47** 1515
Keldysh L V 1965 *Sov. Phys.—JETP* **20** 1018 (Engl. transl.)
- [15] Langreth D C 1976 *1975 NATO Advanced Study Institute on Linear and Nonlinear Transport in Solids* vol B17 (Antwerpen, 1975) (New York: Plenum) pp 3–32
Langreth D C and Wilkins J W 1972 *Phys. Rev. B* **6** 3189
- [16] Mahan G D 1987 *Phys. Rep.* **145** 251
- [17] Araki H and Moriya H 2003 *Rev. Math. Phys.* **15** 93
- [18] Grandy W 1988 *Foundations of Statistical Mechanics (Nonequilibrium Phenomena* vol II) (New York: Springer)
- [19] Anders F B and Schiller A 2005 *Phys. Rev. Lett.* **95** 196801
Anders F B and Schiller A 2006 *Phys. Rev. B* **74** 245113
- [20] Gao S W 1997 *Phys. Rev. Lett.* **79** 3101
Saalfrank P 2006 *Chem. Rev.* **106** 4116
- [21] Hershfield S 1993 *Phys. Rev. Lett.* **70** 2134
- [22] Schiller A and Hershfield S 1995 *Phys. Rev. B* **51** R12896
Schiller A and Hershfield S 1998 *Phys. Rev. B* **58** 14978
- [23] Doyon B and Andrei N 2007 *Phys. Rev. B* **73** 245326
- [24] Gelin M F and Kosov D S 2008 *Phys. Rev. E* **78** 011116
- [25] Dutt P, Koch J, Han J and Hur K L 2011 *Ann. Phys.* **326** 2963
- [26] Han J E 2007 *Phys. Rev. B* **75** 125122
- [27] Gelin M F and Kosov D S 2009 *Phys. Rev. E* **80** 022101
- [28] Lanatà N 2010 *Phys. Rev. B* **82** 195326
- [29] Ng T K 1992 *Phys. Rev. Lett.* **68** 1018
- [30] Heinonen O and Johnson M D 1993 *Phys. Rev. Lett.* **71** 1447
- [31] Bokes P and Godby R W 2003 *Phys. Rev. B* **68** 125414
Bokes P, Mera H and Godby R W 2005 *Phys. Rev. B* **72** 165425
- [32] Caroli C, Combescot R, Nozieres P and Saint-James D 1971 *J. Phys. C: Solid State Phys.* **4** 916
Caroli C, Combescot R, Nozieres P and Saint-James D 1972 *J. Phys. C: Solid State Phys.* **5** 21
- [33] A corresponding continuum version (often termed partition free because the introduction of an initial separation is arbitrary and can have no resulting effect when treating the corresponding formal perturbation to all orders) of the Caroli computational framework [32] is developed in Feuchtwang T E 1974 *Phys. Rev. B* **10** 4121
- [34] Datta S 1990 *J. Phys.: Condens. Matter* **2** 8023
- [35] Wagner M 1991 *Phys. Rev. B* **44** 6104
- [36] Baranger H U and Stone A D 1989 *Phys. Rev. B* **40** 8169
- [37] Hershfield S, Davies J H and Wilkins J W 1991 *Phys. Rev. Lett.* **67** 3720
Hershfield S, Davies J H and Wilkins J W 1992 *Phys. Rev. B* **46** 7046
Hershfield S 1992 *Phys. Rev. B* **46** 7061
- Wilkins J W, Hershfield S, Davies J H, Hyldgaard P and Stanton C J 1992 *Phys. Scr. T* **42** 115
- [38] Meir Y and Wingreen N S 1992 *Phys. Rev. Lett.* **68** 2512
- [39] Landauer R 1957 *IBM J. Res. Dev.* **1** 233
Büttiker M 1986 *Phys. Rev. Lett.* **57** 1761
- [40] Pendry J B, Pretre A B and Krutzen B C H 1991 *J. Phys.: Condens. Matter* **3** 4313
- [41] Davies J H, Hershfield S, Hyldgaard P and Wilkins J W 1993 *Phys. Rev. B* **47** 4603
Hyldgaard P and Lundqvist B I 2000 *Solid State Commun.* **116** 569
- [42] For examples of conserving nonequilibrium Green function studies which determine electron–phonon effects caused by differences in the resonant-level charging along with limitations imposed on the interpretations within a simple Landauer–Büttiker-type description, please see, for example, Hyldgaard P, Hershfield S, Davies J H and Wilkins J W 1994 *Ann. Phys., NY* **236** 1
Ness H, Dash L K and Godby R W 2010 *Phys. Rev. B* **82** 085426
- [43] Vignale G and DiVentra M 2009 *Phys. Rev. B* **79** 014201
- [44] Mera H and Niquet Y M 2010 *Phys. Rev. Lett.* **105** 216408
- [45] Frensley W R 1990 *Rev. Mod. Phys.* **62** 745
- [46] For example, as discussed in Rahman M and Davies J H 1990 *Semicond. Sci. Technol.* **5** 168
- [47] For example, in the quantum cascade laser, Faist J, Capasso F, Sivco D L, Sirtori C, Hutchinson A L and Cho A Y 1998 *Science* **264** 553
- [48] Tome T and de Oliveira M J 2012 *Phys. Rev. Lett.* **108** 020601
- [49] For example, as discussed in Humphrey T E and Linke H 2005 *Phys. Rev. Lett.* **94** 096601 and in references therein
- [50] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
- [51] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
- [52] Mermin N D 1965 *Phys. Rev.* **137** A1441
- [53] Runge E and Gross E K U 1984 *Phys. Rev. Lett.* **52** 997
- [54] Gross E K U and Kohn W 1990 *Adv. Quantum Chem.* **21** 255
- [55] Li T-C and Tong P-Q 1985 *Phys. Rev. A* **31** 1950
- [56] Vignale G and Rasolt M 1987 *Phys. Rev. Lett.* **59** 2360
- [57] DFT has also been generalized to a relativistic description Engels E and Dreizler R M 1996 *Density Functional Theory II* ed R F Nalewajski (Berlin: Springer) pp 1–80
- [58] The action principle of time-dependent DFT can also be used for a formulation of transport within a Liouvillean formulation, Rajagopal A K and Bout F A 1996 *Density Functional Theory II* ed R F Nalewajski (Berlin: Springer) pp 173–209
- [59] Vignale G and Kohn W 1996 *Phys. Rev. Lett.* **77** 2037
Vignale G, Ullrich C A and Conti S 1997 *Phys. Rev. Lett.* **79** 4878
Ullrich C A and Vignale G 2002 *Phys. Rev. B* **65** 245102
- [60] Lüders M, Marques M A L, Lathiotakis N N, Floris A, Profeta G, Fast L, Continenza A, Massidda S and Gross E K U 2005 *Phys. Rev. B* **72** 024545
Marques M A L, Lüders M, Lathiotakis N N, Profeta G, Floris A, Fast L, Continenza A, Gross E K U and Massidda S 2005 *Phys. Rev. B* **72** 024546
- [61] Stefanucci G and Almladh C-O 2004 *Europhys. Lett.* **67** 14
Stefanucci G and Almladh C-O 2004 *Phys. Rev. B* **69** 195318
Kurth S, Stefanucci G, Almladh C-O, Rubio A and Gross E K U 2005 *Phys. Rev. B* **72** 035308
- [62] Gebauer R and Car R 2004 *Phys. Rev. Lett.* **93** 160404
Gebauer R and Car R 2004 *Phys. Rev. B* **70** 125324
- [63] Burke K, Car R and Gebauer R 2005 *Phys. Rev. Lett.* **94** 146803
Koentopp M, Chang C, Burke K and Car R 2008 *J. Phys.: Condens. Matter* **20** 083203

- [64] Hyldgaard P 2008 *Phys. Rev. B* **78** 165109
- [65] Langreth D C, Lundqvist B I, Chakarova-Käck S D, Cooper V R, Dion M, Hyldgaard P, Kelkkänen A, Kleis J, Kong L, Li S, Moses P G, Murray E, Puzder A, Rydberg H, Schröder E and Thonhauser T 2009 *J. Phys.: Condens. Matter* **21** 084203
- [66] Meir Y, Wingreen N S and Lee P A 1991 *Phys. Rev. Lett.* **66** 3048
- [67] Meir Y, Wingreen N S and Lee P A 1993 *Phys. Rev. Lett.* **70** 2601
- [68] Wingreen N S, Jacobsen K W and Wilkins J W 1988 *Phys. Rev. Lett.* **61** 1396
Wingreen N S, Jacobsen K W and Wilkins J W 1989 *Phys. Rev. B* **40** 11834
- [69] Anda E V and Flores F 1991 *J. Phys.: Condens. Matter* **3** 9087
Lake R, Klimeck G and Datta S 1993 *Phys. Rev. B* **47** 6427
Runge E and Ehrenreich H 1992 *Phys. Rev. B* **45** 9145
Runge E and Ehrenreich H 1992 *Ann. Phys., N.Y.* **219** 55
Grein C H, Runge E and Ehrenreich H 1993 *Phys. Rev. B* **47** 12590
- [70] Lesovik G B 1989 *Pis'ma Zh. Eksp. Teor. Fiz.* **49** 513
Lesovik G B 1989 *JETP Lett.* **49** 592 (Engl. transl.)
Yurke B and Kochanski G P 1990 *Phys. Rev. B* **41** 8184
Büttiker M 1990 *Phys. Rev. Lett.* **65** 2901
Landauer R and Martin T 1991 *Physica B* **175** 167
- [71] Runge E 1993 *Phys. Rev. B* **47** 2003
- [72] Davies J H, Hershfield S, Hyldgaard P and Wilkins J W 1992 *Phys. Rev. B* **46** 9620
Hershfield S, Davies J H, Hyldgaard P, Stanton C J and Wilkins J W 1993 *Phys. Rev. B* **47** 1967
- [73] Schiller A and Hershfield S 1996 *Phys. Rev. Lett.* **77** 1821
- [74] Schiller A and Hershfield S 2000 *Phys. Rev. B* **62** R16271
- [75] Plihal M and Gadzuk J W 2001 *Phys. Rev. B* **63** 085404
- [76] Hettler M H, Wenzel W, Wegewijs M R and Schoeller H 2003 *Phys. Rev. Lett.* **90** 076805
Romeike C, Wegewijs M R, Hofstetter W and Schoeller H 2006 *Phys. Rev. Lett.* **96** 196601
- [77] Wacker A, Jauho A-P, Zeuner S and Allen S J 1997 *Phys. Rev. B* **56** 13268
Wacker A and Jauho A-P 1998 *Phys. Rev. Lett.* **80** 369
Lee S C and Wacker A 2002 *Phys. Rev. B* **66** 245314
Weber C, Wacker A and Knorr A 2009 *Phys. Rev. B* **79** 165322
- [78] Thygesen K S and Jacobsen K W 2005 *Chem. Phys.* **319** 146801
Thygesen K S 2006 *Phys. Rev. B* **73** 035309
Thygesen K S 2008 *Phys. Rev. Lett.* **100** 166804
- [79] Mera H, Bokes P and Godby R W 2007 *Phys. Rev. B* **76** 125319
- [80] Wingreen N S, Jauho A-P and Meir Y 1993 *Phys. Rev. B* **48** R8487
Jauho A-P, Wingreen N S and Meir Y 1994 *Phys. Rev. B* **50** 5528
- [81] Nordlander P, Pustilnik M, Meir Y, Wingreen N S and Langreth D C 1999 *Phys. Rev. Lett.* **83** 808
Plihal M, Langreth D C and Nordlander P 2000 *Phys. Rev. B* **61** R13341
Nordlander P, Wingreen N S, Meir Y and Langreth D C 2000 *Phys. Rev. B* **61** 2146
Plihal M, Langreth D C and Nordlander P 2005 *Phys. Rev. B* **71** 165321
- [82] Neaton J B, Hybertsen M S and Louie S G 2006 *Phys. Rev. Lett.* **97** 216405
- [83] Kaasberg K and Flensberg K 2008 *Nano Lett.* **8** 3809
- [84] Thygesen K S and Rubio A 2007 *J. Chem. Phys.* **126** 091101
Thygesen K S and Rubio A 2008 *Phys. Rev. B* **77** 115333
- [85] Myohanen P, Stan A, Stefanucci G and van Leeuwen R 2009 *Phys. Rev. B* **80** 115107
- [86] For example, as summarized in Yasuda H and Sakai A 1997 *Phys. Rev. B* **56** 1069
- [87] Sorbello R S 1997 *Solid State Phys.* vol 51, ed H Ehrenreich and F Spaepen (New York: Academic) pp 159–231
- [88] Gadzuk J W 1970 *Phys. Rev. B* **1** 2110
Gadzuk J W and Holloway S 1986 *Phys. Rev. B* **33** 4298
Gadzuk J W 1991 *Phys. Rev. B* **44** 13466
Gadzuk J W 1993 *Phys. Rev. B* **47** 12832
Gadzuk J W 1995 *Surf. Sci.* **342** 345
- [89] Kumar P and Sorbello R S 1975 *Thin Solid Films* **25** 25
- [90] Sham L J 1975 *Phys. Rev. B* **12** 3142
- [91] Sorbello R S and Dasgupta B B 1980 *Phys. Rev. B* **21** 2196
- [92] Persson B N J and Persson M 1980 *Surf. Sci.* **97** 609
Persson B N J and Persson M 1980 *Solid State Commun.* **36** 175
Persson M and Helsing B 1982 *Phys. Rev. Lett.* **49** 662
- [93] Brandbyge M, Schiøtz J, Sørensen M R, Stoltze P, Jacobsen K W, Nørskov J K, Olesen L, Laegsgaard E, Stensgaard I and Besenbacher F 1995 *Phys. Rev. B* **52** 8499
Sørensen M R, Brandbyge M and Jacobsen K W 1998 *Phys. Rev. B* **57** 3283
- [94] Stipe B C, Rezaei M A, Ho W, Gao S, Persson M and Lundqvist B I 1997 *Phys. Rev. Lett.* **78** 4410
Gao S W, Persson M and Lundqvist B I 1997 *Phys. Rev. B* **55** 4825
Lorente N and Persson M 2000 *Phys. Rev. Lett.* **85** 2997
Lorente N, Persson M, Lauhon L J and Ho W 2001 *Phys. Rev. Lett.* **86** 2593
- [95] Gadzuk J W and Plihal M 2003 *Phys. Rev. B* **68** 235413
- [96] Switching in tunneling systems can be investigated from within a description of the electron–phonon coupling on the transport, Brandbyge M and Hedegård P 1994 *Phys. Rev. Lett.* **72** 2919
- [97] DiVentra M and Pantelides S T 2000 *Phys. Rev. B* **61** 16207
- [98] Todorov T N, Hoekstra J and Sutton A P 2000 *Phil. Mag. B* **80** 421
Sutton A P and Todorov T N 2004 *Mol. Phys.* **102** 919
- [99] Todorov T N 2001 *J. Phys.: Condens. Matter* **13** 10125
- [100] Todorov T N 2002 *J. Phys.: Condens. Matter* **14** 3049
- [101] Narayanamurti V 1981 *Science* **213** 717
- [102] A possible mechanism for frequency-selective control of current-induced vibrational (or optical) excitations in tunneling is described in Hyldgaard P 2001 *Low Temp. Phys.* **27** 585
Hyldgaard P 2003 *Mater. Sci. Eng. C* **23** 243
- [103] DiVentra M, Chen Y-C and Todorov T N 2004 *Phys. Rev. Lett.* **92** 176803
- [104] Verdozzi C, Stefanucci G and Almladh C-O 2006 *Phys. Rev. Lett.* **97** 046603
- [105] Frederiksen T, Paulsson M, Brandbyge M and Jauho A-P 2007 *Phys. Rev. B* **75** 205413
- [106] Dundas D, McEniry E J and Todorov T N 2009 *Nature Nanotechnol.* **4** 99
- [107] Todorov T N, Dundas D and McEniry E J 2010 *Phys. Rev. B* **81** 075416
- [108] Wang Y F, Kröger J, Berndt R, Vazquez H, Brandbyge M and Paulsson M 2010 *Phys. Rev. Lett.* **104** 176802
- [109] Bode N, Kusminskiy S V, Egger R and von Oppen F 2011 *Phys. Rev. Lett.* **107** 036804
- [110] Lü J-T, Brandbyge M and Hedegård P 2010 *Nano Lett.* **10** 1657 (details on the current description are given in the supplementary material)
- [111] For example, Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
- [112] Rydberg H, Lundqvist B I, Langreth D C and Dion M 2000 *Phys. Rev. B* **62** 6997

- Rydberg H, Dion M, Jacobson N, Schröder E, Hyldgaard P, Simak S I, Langreth D C and Lundqvist B I 2003 *Phys. Rev. Lett.* **91** 126402
- Dion M, Rydberg H, Schröder E, Langreth D C and Lundqvist B I 2004 *Phys. Rev. Lett.* **92** 246401
- Dion M, Rydberg H, Schröder E, Langreth D C and Lundqvist B I 2005 *Phys. Rev. Lett.* **95** 109902(E)
- Román-Peréz G and Soler J M 2009 *Phys. Rev. Lett.* **103** 096102
- Gulans A, Puska M J and Nieminen R M 2009 *Phys. Rev. B* **79** 201105
- Cooper V R 2010 *Phys. Rev. B* **81** 161104
- Klimes J, Bowler D R and Michaelides A 2010 *J. Phys.: Condens. Matter* **22** 022201
- Lee K, Murray E D, Kong L, Lundqvist B I and Langreth D C 2010 *Phys. Rev. B* **82** 081101
- [113] Thonhauser T, Cooper V R, Li S, Puzder A, Hyldgaard P and Langreth D C 2007 *Phys. Rev. B* **76** 125112
- [114] Kohn W, Meir Y and Makarov D E 1998 *Phys. Rev. Lett.* **80** 4153
- Kurth S and Perdew J P 1999 *Phys. Rev. B* **59** 10461
- Dobson J F and Wang J 1999 *Phys. Rev. Lett.* **82** 2123
- Dobson J F and Dinte B P 1996 *Phys. Rev. Lett.* **76** 1780
- Pitarke J M and Perdew J P 2003 *Phys. Rev. B* **67** 045101
- Vydrov O A and Van Voorhis T 2009 *Phys. Rev. Lett.* **103** 063004
- Vydrov O A and Van Voorhis T 2010 *J. Chem. Phys.* **133** 244103
- [115] For example, Tkatchenko A, Romaner L, Hoffman O, Zojer E, Ambrosch-Draxl C and Scheffler M 2010 *MRS Bull.* **35** 435
- Grimme S 2011 *Comput. Mol. Sci.* **1** 211
- [116] Ahlrichs R, Penco R and Scoles G 1977 *Chem. Phys.* **19** 119
- Wu Q and Yang W 2002 *J. Chem. Phys.* **116** 515
- Grimme S 2004 *J. Comput. Chem.* **25** 1463
- Jurecka P, Cerny J, Hobza P and Salahub D R 2007 *J. Comput. Chem.* **28** 555
- Grimme S, Antony J, Schwabe T and Mück-Lichtenfeld C 2007 *Org. Biomol. Chem.* **5** 741
- Morgado C, Vincent M A, Hiller I H and Shan X 2007 *Phys. Chem. Chem. Phys.* **9** 448
- Pavone M, Rega N and Barone V 2008 *Chem. Phys. Lett.* **452** 333
- Tkatchenko A and Scheffler M 2009 *Phys. Rev. Lett.* **102** 073005
- Kannemann F O and Becke A D 2010 *J. Chem. Theory Comput.* **6** 1081
- Grimme S, Antony J, Ehrlich S and Krieg H 2010 *J. Chem. Phys.* **132** 1541004 and references therein
- [117] Messiah A 1961 *Quantum Mechanics* vol II (Amsterdam: North-Holland) chapter XVII, section 13, and chapter XVIII, sections 14–16
- [118] Lang N D 1995 *Phys. Rev. B* **52** 5335
- [119] Di Ventura M, Pantelides S T and Lang N D 2000 *Phys. Rev. Lett.* **84** 979
- [120] Brandbyge M, Mozos J L, Ordejón P, Taylor J and Stokbro K 2002 *Phys. Rev. B* **65** 165401
- Artacho E, Gale J D, Garcia A, Junquera J, Ordejón P and Sánchez-Portal D 2002 *J. Phys.: Condens. Matter* **14** 2745
- [121] Havu P, Havu V, Puska M J and Nieminen R M 2004 *Phys. Rev. B* **69** 115325
- Havu P, Puska M J, Nieminen R M and Havu V 2004 *Phys. Rev. B* **70** 233308
- Havu P, Tuomisto N, Väänänen R, Puska M J and Nieminen R M 2005 *Phys. Rev. B* **71** 235301
- [122] Enkovaara J *et al* 2010 *J. Phys.: Condens. Matter* **22** 3202
- Strange M, Kristensen I S, Thygesen K S and Jacobsen K W 2008 *J. Chem. Phys.* **128** 4714
- [123] Lippmann B A and Schwinger J 1950 *Phys. Rev.* **79** 469
- [124] Messiah A 1961 *Quantum Mechanics* vol II (Amsterdam: North-Holland) chapter XIX, section 3
- [125] Crommie M F, Lutz C P and Eigler D M 1993 *Nature* **363** 524
- Heller E J, Crommie M F, Lutz C P and Eigler D M 1994 *Nature* **369** 464
- [126] Repp J, Moresco F, Meyer G, Rieder K-H, Hyldgaard P and Persson M 2000 *Phys. Rev. Lett.* **85** 2981
- [127] Eigler D M, Lutz C P and Rudge W E 1991 *Nature* **352** 600
- Dujardin G, Walkup R E and Avouris Ph 1992 *Science* **255** 1232
- [128] Svensson K, Olin H and Olsson E 2004 *Phys. Rev. Lett.* **93** 145901
- [129] Hyldgaard P and Wilkins J W 1996 *Phys. Rev. B* **53** 6889
- [130] See, for example, Doniach S and Sonnheimer E H 1982 *Green's Functions for Solid State Physicists* (Redwood City, CA: Addison-Wesley) pp 81–5
- Mahan G D 1981 *Many-Particle Physics* (New York: Plenum) pp 234–7
- [131] Hershfield S P 1993 private communication
- Hershfield S P 2000 personal communication
- [132] Dyson F J 1949 *Phys. Rev.* **75** 486
- [133] Pirenne J 1948 *Helv. Phys. Acta* **21** 226
- Pirenne J 1952 *Phys. Rev.* **86** 395
- [134] Gellmann M and Goldberger M L 1953 *Phys. Rev.* **91** 398
- [135] DeWitt B S 1955 *Phys. Rev.* **100** 905
- [136] Langreth D C 1964 Theory of polaron mobility *PhD Thesis* University of Illinois
- [137] Langreth D C 1966 *Phys. Rev.* **150** 516
- [138] Messiah A 1961 *Quantum Mechanics* vol II (Amsterdam: North-Holland) chapter XIX
- [139] Di Ventura M, Pantelides S T and Lang N D 2002 *Phys. Rev. Lett.* **88** 046801
- Di Ventura M, Pantelides S T and Lang N D 2002 *Phys. Rev. Lett.* **89** 139902(E)
- [140] Brandbyge M, Stokbro K, Taylor J, Mozos J L and Ordejón P 2003 *Phys. Rev. B* **67** 193104
- [141] Merzbacher E 1970 *Quantum Mechanics* (New York: Wiley) p 41
- [142] Dashen R, Ma S-K and Bernstein H J 1969 *Phys. Rev.* **187** 345
- [143] Langer J S and Ambegaokar V 1961 *Phys. Rev.* **121** 1090
- [144] Messiah A 1961 *Quantum Mechanics* vol I (Amsterdam: North-Holland) chapter III
- [145] Messiah A 1961 *Quantum Mechanics* vol I (Amsterdam: North-Holland) chapter X, sections 17 through 20
- [146] See, for example, Doniach S and Sonnheimer E H 1982 *Green's Functions for Solid State Physicists* (Redwood City, CA: Addison-Wesley)
- [147] Hyldgaard P and Persson M 2000 *J. Phys.: Condens. Matter* **12** L13
- [148] Kadanoff L P and Baym G 1962 *Quantum Statistical Mechanics* (New York: Benjamin) chapter 2
- [149] Zaramba E and Kohn W 1977 *Phys. Rev.* **15** 1769
- [150] Harris J and Liebsch A 1982 *J. Phys. C: Solid State Phys.* **15** 2275
- Liebsch A, Harris J, Salanon B and Lapujolade J 1982 *Surf. Sci.* **123** 338
- Nordlander P, Holmberg C and Harris J 1986 *Surf. Sci.* **175** L753
- [151] Harris J 1985 *Phys. Rev. B* **31** 1770
- [152] Grimley T B 1967 *Proc. Phys. Soc.* **90** 751
- [153] Einstein T L and Schrieffer J R 1973 *Phys. Rev. B* **7** 3629
- Einstein T L 1978 *Surf. Sci.* **75** L497
- Einstein T L 1996 *Handbook of Surface Science* vol 1, ed W Unertl (Amsterdam: Elsevier) chapter 11
- [154] Lau H and Kohn W 1978 *Surf. Sci.* **75** 69
- [155] Hyldgaard P and Einstein T L 2002 *Europhys. Lett.* **59** 265
- [156] Lloyds P 1967 *Proc. Phys. Soc.* **90** 207

- [157] Hyldgaard P 2012 unpublished
- [158] Lighthill M J 1964 *Introduction to Fourier Analysis and Generalized Functions* (London: Cambridge University Press)
- [159] Inglesfield J E 1981 *J. Phys. C: Solid State Phys.* **14** 3795
Nekovee M and Inglesfield J 1992 *Europhys. Lett.* **19** 535
Szunyogh L, Újfalussy B, Weinberger P and Kollár J 1994 *Phys. Rev. B* **49** 2721
Ishida H 2001 *Phys. Rev. B* **63** 165409
Butti G, Caravati S, Brivio G P, Trioni M I and Ishida H 2005 *Phys. Rev. B* **72** 125402
- [160] Landau L D and Lifshitz E M 1980 *Statistical Physics* 3rd edn, part 1 (Oxford: Pergamon) pp 158–9
- [161] Zheng X, Wang F, Yam C Y, Mo Y and Chen G 2007 *Phys. Rev. B* **75** 195127
- [162] van Leeuwen R 1999 *Phys. Rev. Lett.* **82** 3863
- [163] Lee K, Kelkkanen A K, Berland K, Andersson S, Langreth D C, Schröder E, Lundqvist B I and Hyldgaard P 2011 *Phys. Rev. B* **84** 193408
- [164] Ashcroft N W and David Mermin N 1976 *Solid State Physics* (New York: Holt, Rinehart, and Winston) p 772
- [165] For example, Gross E K U, Dobson J F and Petersilka M 1996 *Density Functional Theory II* ed R F Nalewajski (Berlin: Springer) p 96
- [166] Koentopp M, Chang C, Burke K and Car R 2008 *J. Phys.: Condens. Matter* **20** 083203
- [167] Messiah A 1961 *Quantum Mechanics* vol II (Amsterdam: North-Holland) chapter XIX, section 29
- [168] Berland K, Einstein T L and Hyldgaard P 2012 *Phys. Rev. B* **85** 035427
- [169] Hauge E H and Støvneng J A 1989 *Rev. Mod. Phys.* **61** 917