Potential-Energy Surfaces for Excited States in Extended Systems

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With a simple, physically intuitive and detailed method, first-principles calculations of potential energy surfaces (PES) are performed for excited states in a number of illustrative systems including, dimers (H_2 and NaCl) and gas-surface systems (Cl/Na(100) and Cl_2/Na(100)). For more complex systems, where reliable first-principle methods to account for electronically excited states have so far been absent, our method is very promising. The method is based on density functional theory and is a generalization of the ΔSCF method, where electron-hole pairs are introduced in order to model excited states, corresponding to internal charge transfers in the considered system. The desired excitations are identified by analysis of calculated electron orbitals, local densities of states and charge densities. The calculated results are in promising agreement with those of other studies.

I. INTRODUCTION

Description of, e.g., gas-surface processes calls for a theoretical account of not only ground-state properties of the system but also excited states and transitions among these states. *Density Functional Theory* (DFT)[1,2] is an important and significant tool for ground-state and equilibrium properties of atoms, molecules, surfaces, and materials, with a good accuracy.[3] Although DFT has proven very useful for calculating ground-state potential-energy surfaces (PES), practical theoretical methods for electronically excited states are still largely absent for many-electron systems. Yet such excited states are abundant, let it be in ionization of atoms and molecules, optical processes of solids, photo-stimulated surface-, materials-, and nano-processes, and gas-surface dynamics. This paper is addressed to the calculation of PES for excited states in extended systems, in particular those that are useful in a diabatic descriptions of dynamical surface processes.

The standard description of electronic ground-state properties of materials utilizes the Born-Oppenheimer approximation (BOA).[4] This approximation defines the stationary adiabatic states[5,6] of a many-electron system. It approximates the PES for the nuclei by giving the eigenvalues of the electronic part (H_e) of the total Hamiltonian, defined for each fixed internuclear separation ($\{R\}$). This implies that electronic transitions between different electronic states are neglected. The adiabatic description fully accounts for several experimentally observed phenomena in gas-surface reactions, such as adsorption-site geometry and bond characterization, dissociation, vibrational energies of atoms and molecules on metal surfaces, epitaxial growth processes, and interpretation of STM images and STM-observed processes.[7]

Although the BOA is normally a good approximation, its validity is questioned in basically three situations: (i) when the time scales for the motion of the electrons and nuclei are comparable, (ii) when the energy separation between the electronic states are small, i.e. transitions among the electronic states cannot be neglected, and (iii) when, due to a poor choice of the basis functions, the adiabatic PES suffers an avoided crossing.

All of these difficulties can be circumvented by making an obvious and reasonable definition of the basis functions that has the virtue of preserving the essential distinction between nuclei and electrons, which is the key ingredient in the BOA. Such alternative definitions of electronic states, which are called *diabatic states*,[5,6] lead to non-diagonal representations of H_e and take into account transitions between different electronic states. They are particularly interesting for systems, where non-adiabatic processes have been observed experimentally.[8,9]

Here, these features are illustrated in a number of model cases. The "ultimate" model case is the interaction between individual Na and I atoms,[10] where charge transfer and curve crossing are key and obvious ingredients. In the dissociation of Cl_2 on the K surface,[11–13] a non-adiabatic scenario provides an explanation for the observed exoelectron emission and surface chemiluminescence.[11]

Our primary motivation for this study is an improved understanding of oxidation of metals. In the initial step, the sticking behavior of the O_2 molecule on the Al(111) surface[14] is not understood in an adiabatic picture,[15–17] and a non-adiabatic process is suggested.[18] Unfortunately the calculation of diabatic states is not straightforward and has traditionally quite a high degree of empirical input. While useful, such an approach is neither necessarily predictive in nature nor unique in its choice of diabatic states.

Unfortunately standard DFT, with its success in describing adiabatic processes, fails to account for diabatic ones, involving electronically excited states. It has, however, some limited but exact results on excited states: The Hohenberg-Kohn theorems can be applied to the excited states that have the lowest energy in each given overall symmetry.[19,20] As diabatic PES's are important in understanding such surface processes as chemiluminescence,[11,21] sticking,[14,18] electron- or photon-stimulated desorption,[22] abstraction,[23] *i.e.* emission of atoms upon dissociative molecular adsorption, a simple, intuitive and DFT-based method for obtaining them from first-principle should be very useful.

There are some attempts to deal with excitations on the basis of DFT, like *GW* approximation,[24–26] Görling-Levy perturbation theory,[27–29] time-dependent DFT (TDDFT),[30–32] and ΔSCF.[19,20,33–35]

The *GW* approximation[24–26,36] uses properties of the single- and two-particle Green's functions to obtain excitation energies. Excitations from the one-particle Green's function include ionization[37] and photoemission[38] processes, while the two-particle Green's function, representing electron-hole excitations,[25,37,39] gives information about internal excitations in atoms, molecules, and clusters.

In the Görling-Levy perturbation theory[27–29] the energy functionals are expressed not only in terms of the density but also in terms of the Kohn-Sham (KS)-orbitals. This improves the description of the functionals and thus their corresponding KS-orbitals. The eigenvalues corresponding to the improved KS-orbitals are used successfully to calculate excitations within the system under consideration, as the eigenenergy difference between an occupied and an unoccupied KS-orbital. This method is typically applied to the ionization of atoms, with a very good accuracy.[29]

The time-dependent extension of DFT (TDDFT),[30–32] which has received extensive attention, is in principle an exact theory for the description of internal excitations. It uses the frequency-dependent polarizability of an electronic system and relates the excitation in that system to the poles of its polarizability. In this way the excitation energies are found to be the eigenenergies of a matrix of both occupied and unoccupied KS-orbitals. Promising results are obtained for the lowest excitations in atoms,[40] molecules,[40,41] and even some extended systems.[42]

The ΔSCF utilizes the Hartree-Fock approximation (HFA)[43] or its natural extensions and is extensively applied to atoms, molecules and clusters. Being finite in size, these systems have discrete eigenstates, where electronic configurations are easy to write down. The excitation energies are found by means of self-consistent-field (SCF) calculations for different electronic configurations. The calculations are straightforward for an electronic configuration represented by a single determinant. On the other hand, the so-called "sum-method"[44] is applied to multiple states. Simply, it means that a linear combination of determinants is constructed into a mixed state that can be described by a single determinant. If the energy of all the involved determinants, except for one, are known excitation energy of the unknown state can be extracted. The ΔSCF method is easy to generalize to DFT, where the different electronic configurations in the KS formulation are constructed by a set of KS-orbitals. So far the application of this method to excited state in general has been formally unjustified, the only exception being the lowest ones in each symmetry.[19,20] In a recent article by Görling,[35] where the KS formalism is extended to include also excited states, the ΔSCF method for general excited states gets formal justification.

Despite these encouraging efforts to deal with excited states in different electronic systems, there is in the literature no DFT-based first-principles calculation made on such systems as a molecule at the vicinity of a surface. The above-mentioned methods, in their present form, seem to be too difficult to apply for such complex systems.

In this paper a DFT-adapted ΔSCF method is developed. Using this method PES's of electronically excited states in extended systems are calculated, in particular the diabatic PES's in molecule-surface reactions. The method utilizes three main concepts, namely: (i) interpretation of the KS-orbitals in a molecular orbital (MO) scheme, (ii) discretization of these orbitals and their energy levels, using supercell calculations with periodic boundary conditions, and (iii) introduction of electron-hole (e-h) pair excitations in the system, which is equivalent to an internal charge-transfer in the supercell. First a standard DFT calculation is performed to obtain the adiabatic ground-state PES of the system and the KS-orbitals with discrete energy levels. Then the relevant KS-orbitals for the desired internal charge transfer process are identified as the ones that should be occupied in the ground-state but unoccupied in the excited electronic configuration. This requires a thorough analysis of the local density of states (LDOS). Further, a hole is introduced into one of these occupied KS-orbitals together with an extra electron into another one that is introduced to the excited configuration. Finally, the total electronic system is allowed to relax self-consistently in a way that keeps the hole in the same KS-orbital. The total energy difference between the excited- and ground-state configurations is identified as the excitation energy.

In order to test our method, it is applied to a number of characteristic systems. These include the H_2 molecule, the NaCl dimer, and the gas-surface systems Cl/Na(100) and Cl_2/Na(100). The complexity of the test systems is increased step by step, which illustrates the power of our method to be applicable on a wide and diverse range of systems, with a useful accuracy. When comparison is possible it is shown that the results are in good agreement with those from other calculations and empirical deductions, which gives confidence in using our method to other molecule-surface systems as well.

The organization of the paper is as follows. In section II the theory is described. The calculational method and the implementation of the theory are given in section III. Results from the calculations are presented in section IV, while the discussion is in section V. The paper is ended by conclusions and outlooks, given in section VI.

II. THEORETICAL MODEL

The Hohenberg-Kohn theorem states that the total energy of the electronic system is characterized by just the electron density $\rho(\mathbf{r})$ and the external potential $v_{ext}(\mathbf{r})$. This implies that the Hamiltonian for the electronic system is given by[1]

$$H[\rho(\mathbf{r})] = \int d\mathbf{r}\rho(\mathbf{r})v_{ext}(\mathbf{r}) + F[\rho(\mathbf{r})], \tag{2.1}$$

where $F[\rho(\mathbf{r})]$ is a universal functional of the density. There exist different possible representations for the functional $F[\rho(\mathbf{r})]$. An explicit form for it is given by the KS representation[2] as

$$F[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho(\mathbf{r})], \tag{2.2}$$

where $T_s[\rho(\mathbf{r})]$ is the kinetic-energy functional of independent electrons in the KS model system, $\frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$ is the Hartree term, describing the electron-electron repulsion, while all of the many-body effects are included in the exchange-correlation functional $E_{xc}[\rho(\mathbf{r})]$. In the KS formalism one-particle eigenfunctions $\{\varphi_i(\mathbf{r})\}$, where $\mathbf{r}$ denotes both the spatial and spin coordinate, are introduced. These are the KS-orbitals mentioned in the introduction. An electronic configuration of a system is defined by occupying N KS states corresponding to N electrons. In contrast to any excited electronic configuration, the ground state is uniquely represented by the N lowest KS states. The electronic density $\rho(\mathbf{r})$ is constructed by summing over the N lowest KS states corresponding to N electrons, according to

$$\rho(\mathbf{r}) = \sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2. \tag{2.3}$$

The ground state energy E_0 and density $\rho_0(\mathbf{r})$ are then obtained by minimizing the functional given in Eq. (2.1) with respect to the $\{\varphi_i(\mathbf{r})\}$, which gives the following equations for the KS-orbitals

$$\{-\frac{1}{2}\nabla^2 + v_{ext}[\rho] + v_H[\rho] + v_{xc}[\rho]\}\varphi_i = \epsilon_i\varphi_i. \tag{2.4}$$

Here the effective potentials $v_{ext}[\rho(\mathbf{r})]$, $v_H[\rho(\mathbf{r})]$, and $v_{xc}[\rho(\mathbf{r})]$ are the functional derivatives of the corresponding energy functional.

In the standard interpretation of DFT the set of KS energy-parameters ϵ_i have no physical meaning except for the highest occupied one, which represents the ionization energy.[20,45] However, it is clear that the KS-orbitals describe non-interacting electrons in an exchange-correlation potential and can be used to define an electronic configuration. This means that, in order to lower the total energy in the electronic system, the KS-orbitals describe the formation of bonds and other physically important effects.

A natural and intuitive way to introduce a certain excitation into the system is to use the concept of electron-hole (e-h) pairs, i.e. charge transfer between occupied and unoccupied KS-orbitals. In order to create such e-h pairs in the system, we need to change occupancies by unity. For a finite system, like an atom or molecule, this is done easily, as each specified orbital has only one energy level. For extended systems, however, the energy levels are so densely packed that a confinement treatment is usually made. Here a practical method is proposed to construct e-h-pair excitations by using the standard supercell description, with its finite number of discrete k states. Having obtained the electronic ground-state configuration with a set of occupied KS-orbitals, an e-h pair is introduced by emptying one of the occupied orbitals and filling one of the unoccupied orbitals. Technically, occupation numbers n_i are assigned to each KS-orbital φ_i, with n_i=0 representing an empty orbital and n_i=1 an occupied orbital. Using the occupation numbers, the charge density given in Eq. (2.3) is modified to

$$\rho(\mathbf{r}) = \sum_{i=1}^{\infty}n_i|\varphi_i(\mathbf{r})|^2 \tag{2.5}$$

and the charge density of the excited state becomes

$$\tilde{\rho}(\mathbf{r}) = \sum_{i=1}^{\infty}n_i|\tilde{\varphi}_i(\mathbf{r})|^2. \tag{2.6}$$

Here the KS-orbitals $\tilde{\varphi}_i(\mathbf{r})$ describe the new excited KS system, calculated in a self-consistent way with $n_k = 0$ for some $k \leq N$, and where KS-orbitals $\varphi_{k'}$ that are unoccupied in the ground state now are included ($n_{k'} = 1$).

The potential constructed from the excited electronic density is then used in setting up new KS equations,

$$\{-\frac{1}{2}\nabla^2 + \tilde{v}_{ext}[\tilde{\rho}] + \tilde{v}_H[\tilde{\rho}] + \tilde{v}_{xc}[\tilde{\rho}]\}\tilde{\varphi}_i = \tilde{\epsilon}_i\tilde{\varphi}_i, \tag{2.7}$$

which are solved self-consistently with the only new restriction of keeping the hole in the affected KS-orbital φ_k. Since the effective potential depends on excited KS orbitals, $\tilde{\varphi}_i(\mathbf{r})$, all effects from the excitation are dealt with self-consistently. The energy for the electronically excited system is evaluated in the usual minimization procedure for the energy functional given in Eq. (2.1), with the electron density of the excited system $\{\tilde{\rho}(\mathbf{r})\}$ as the input.

In a practical situation, a particular e-h-pair excitation is searched for. For instance, in Na + Cl, the charge transfer from the covalent state should be an electron going from Na to Cl. Thus, one has to look at the character of the KS-orbitals $\{\varphi_k\}$ and identify the electron and hole orbitals that are primarily active in the transfer. In a general case, such an identification is hard to do in a unique way. For diabatic states, the identification is eased by considering the electronic structure for the involved entities at extreme values of the nuclear coordinates.

A justification for this method based on the original Hohenberg-Kohn theorem[1] has been lacking until recently, where an article by Görling[28] provides a formal justification. Reference[28] points out that the exact exchange-correlation functional and a generalized adiabatic connection (GAC) between the KS-system and the real system are required to ensure that the excitation energy is correctly calculated. In this paper both of these important points are ignored. The ignorance of GAC will be remedied by a thorough examination of the calculated properties of the excited state.

III. CALCULATION METHOD

The first-principles calculations presented in this paper are based on the modified DFT described in the previous section and outlined in detail below. They are performed with the plane-wave pseudopotential code `DACAPO`.[46] For the exchange-correlation energy-density functional the generalized-gradient (GGA) approximation[47–49] in the PW91[47] version is used. The wave functions are expanded in a plane-wave basis set, and the electron-ion interactions are described by ultrasoft pseudopotentials.[50] The KS equations, Eqs. (2.4) and (2.7), are solved by using the density-mix scheme,[51] in which the electronic density between iterations is updated by means of a Pulay-mixing algorithm. The occupation numbers are updated using a technique based on minimization of the free energy functional. The k-points are chosen with the Monkhorst-Pack[52] method. All calculations are performed with allowance for spin polarization.

In order to calculate the energy for an excited state, first a standard ground-state DFT calculation is performed, using the supercell method. For each k-point this yields a set of KS-orbitals and their corresponding discrete eigenenergies. The second step is to identify the occupied KS-orbital that should be unoccupied in the desired excited state, had it not occurred an internal charge transfer from the excited state to the ground state. This orbital is referred to as the KS-hole in the following. For each k-point the identification of the KS-hole is achieved by analyzing the local density of states (LDOS) projected on the orbitals of the unit under consideration. Indeed, the LDOS is a necessary tool to make the identification, especially for extended systems. The hole is introduced in the chosen KS-orbital by setting the occupation number for that KS-orbital equal to zero.

In practice, the use of several k points to sample the k space causes only minor difficulties in creating the e-h pairs. If the correct KS-orbital can be found for one k point, the same procedure can be used for all the other k points. This is due to the fact that for each k point the KS-orbitals and their corresponding eigenenergies are still discrete.

In the third step, a self-consistent-field (SCF) calculation with the new set of occupied KS-orbitals is performed in such a way that all the electronic degrees of freedom except for the KS-hole are allowed to relax. Finally the excitation energy is evaluated as the difference between total energies for the excited- and ground-state configurations, respectively. The correctness of the identification of the KS-hole is checked by analyzing cuts of the charge density in the supercell for the ground- and excited-state calculations. If the calculated charge density for the excited state does not correspond to the desired excitation, the second and third procedures are repeated with a new KS-hole.

The calculations in the two dimer test cases (H_2 and NaCl) are performed with a supercell having a volume of $20\times20\times20$ Å^3, in order to minimize the overlap effect from the periodicity of the supercell. For these two test cases, a cutoff energy of 25 Ry with 1 irreducible k-point sampling are used. The gas-surface systems (Cl/Na(100) and Cl_2/Na(100)) are described by a slab geometry of four Na layers and five vacuum layers. Here the cutoff energy is 25 Ry and 10 irreducible k points are used. The Cl atom and the Cl_2 molecule are adsorbed on one side of the slab only. The induced dipole moment is compensated for by an effective dipole correction.[53]

IV. RESULTS

Calculations have been performed for a number of test systems. Here the results for total energies and various aspects of the electron structure, such as the charge densities for both the ground and the excited states, are presented. Discussions of possible limitations of the method for the systems studied here as well as its use for other molecule-surface systems are left for the next section.

A. H_2 molecule

The H_2 molecule serves as a simple yet interesting test system. There are two electrons in the system, and the formation of the hydrogen molecule bond is well-known.[54] For the H_2 molecule quite a number of calculations have been made for both ground- and excited-states.[41,55,56] In an LCAO (linear combination of atomic orbitals) picture, the two s-orbitals of the hydrogen atoms combine and form two σ bonds, one bonding (1σ) and one antibonding ($1\sigma^*$). The σ orbitals are completely degenerate with respect to spin, which implies that the total spin S is equal to 0 in the H_2 ground state and 0 or 1 for excited states, with one electron in the bonding and one in the antibonding molecular orbital.

The $^1\Sigma$ ground state of the hydrogen molecule is calculated with the standard DFT at different separations (see Fig 1a). The equilibrium bond length is calculated to be 0.75 Å, in excellent agreement with other calculations.[41,55,56] To obtain the energetically lowest excited state (the desired excited state) a KS-hole is introduced in one 1σ orbital and one electron is put into a $1\sigma^*$ orbital, and the electronic system (except for the KS-hole) is allowed to relax completely. The self-consistent solution shows the extra electron to be placed in the same spin channel as the other one. This makes the excited state a spin triplet (S = 1), in agreement with Hund's spin rule. Furthermore, the excited $^3\Sigma$ state has repulsive character, as expected. The calculated energy for the excited state at different separations is illustrated in Fig. 1a and agrees well with other calculations,[41,55,56] see Fig. 1b. The potential energies for the excited $^3\Sigma$ and ground $^1\Sigma$ state decrease and increase, respectively, with growing intermolecular separation. This is expected, since the energy difference between both hydrogen atoms having the same or the opposite spin should vanish at infinity separation.

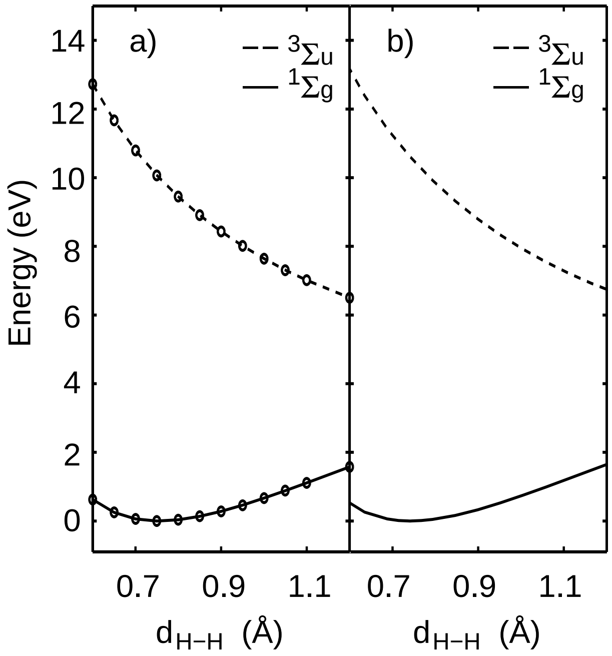

FIG. 1. The energy for the $^1\Sigma_g$ ground-state (solid line) and the $^3\Sigma_u$ exited state (dashed line) for the H_2 molecule as a function of bond length d_{H-H} from (a) DFT calculations and (b) calculations done with CI studies.[55]

Figure 2 shows charge-density difference between the excited $^3\Sigma_u$ state and the ground $^1\Sigma_g$ state along the axis of the hydrogen molecule in two parts: (a) shows the depletion in the charge density, while (b) shows the replacement of the depleted charge due to the e-h excitation introduced into the system. From (a) it is clear that charge is removed from the center of the hydrogen molecule in agreement with placing a hole in a binding σ orbital. In (b) the charge is placed around the hydrogen atoms indicating that the bond between the hydrogen atoms is diminished as expected with one electron placed in an anti-binding σ^* orbital.

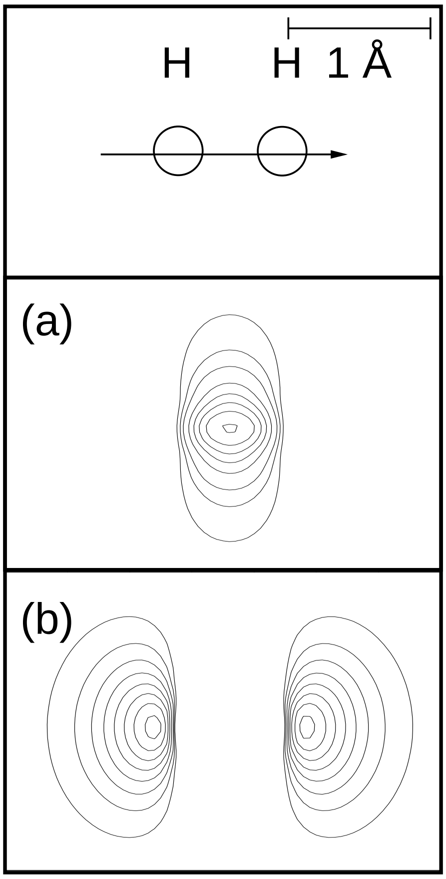

FIG. 2. The H_2 charge-density difference between the excited $^3\Sigma_u$ state and the ground $^1\Sigma_g$ state is calculated and it's profile along the axis of the hydrogen molecule is plotted in two parts: (a) shows the depletion in the charge density, while (b) shows the replacement of the depleted charge due to the e-h excitation introduced in the system.

B. NaCl dimer

In contrast to the H_2 molecule, the electronic ground state of the NaCl dimer is ionic, with the Na and Cl atoms being positively and negatively charged, respectively. At infinite separations, the relevant energy is set by the difference between the ionization energy for the Na atom and the affinity energy for the Cl atom which is about 1.4 eV. An internal charge transfer is energetically unfavorable here and the ionic potential is lying 1.4 eV above the "covalent" one. At some intermediate separation ($\sim$ 10 Å)[57] the PES's for the ionic and covalent states have the same energy, leading to a curve crossing, which makes an internal charge transfer feasible. Figure 3 shows the calculated potential energies for the ionic ground state with an equilibrium bondlength of 2.3 Å, and the covalent excited $^1\Sigma$ state. The ground-state calculation yields an electronic configuration of $3p^6$ for the Cl atom, consistent with the charge transfer concept. In order to calculate the covalent excited state, the hole is introduced in one of the p KS-orbitals. In the self-consistent calculation for the excited state the extra electron is put in the same spin channel as for the KS-hole, according to Hund's rule, giving the triplet $^3\Sigma$ state. Next, the extra electron is placed in the opposite spin channel compared to the KS-hole, giving rise to a mixed multiple state. According to the "sum-method" the energy of the excited singlet $^1\Sigma$ state is extracted from the calculated energy of the mixed state. The energy separation between the singlet and triplet state is calculated to be in the order of 0.15 eV. It should be emphasized that all the electronic degrees of freedom are dealt with self-consistently, except for the KS-holes. For comparison, both theoretical and experimentally measured[59] (crooses in Figure 3a and 3b) values are shown. The ionic ground-state and excited $^1\Sigma$ state calculated using semi-empirical valence-bond method[57] is shown in Figure 3b.

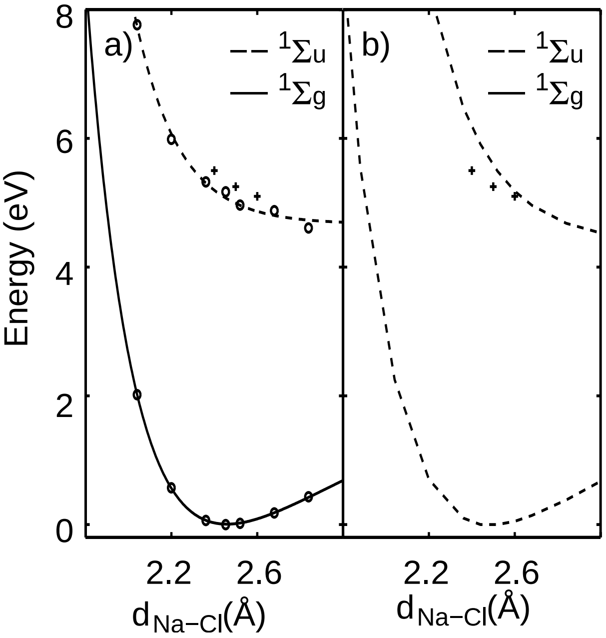

FIG. 3. The energy for the ionic $^1\Sigma$ ground-state (solid line) and the $^1\Sigma$ excited state (dashed line) for the NaCl dimer, as a function of bond length $d_{\mathrm{Na-Cl}}$ from (a) DFT calculations, and (b) calculations of the ionic $^1\Sigma$ ground- and $^1\Sigma$ excited state done by valence bond method.[57] The experimentally measured values[59] are represented as crosses in both (a) and (b).

The charge density difference between the covalent $^3\Sigma$ excited state and the ionic $^1\Sigma$ ground-state is calculated and its profile along the axis of the NaCl dimer is plotted in two parts in Figure 4: (a) shows the depletion in the charge density, while (b) shows the replacement of the depleted charge due to the e-h excitation introduced in the system. (a) shows that the depletion of charge is focused around the Cl atom and mostly in the direction of the dimer axis, in agreement with the removal of an ionic bond. From (b) we see that the charge is placed in such a fashion that the charge around the Cl atom becomes more spherical but it is also placed around the Na atom. The charge density profile corresponds to a neutral Cl atom and and a weakly bound s-electron configuration of the Na atom.

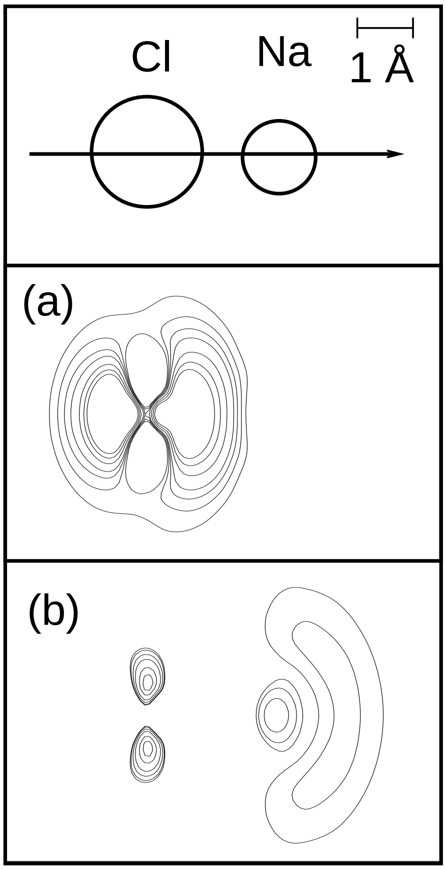

FIG. 4. The NaCl charge-density difference between the covalent $^3\Sigma$ excited state and the ionic $^1\Sigma$ ground-state is calculated and its profile along the axis of the NaCl dimer: (a) the depletion in the charge density, while (b) the replacement of the depleted charge due to the e-h excitation introduced in the system.

C. Cl on the Na(100) surface

The complexity in finding the right KS-orbital is radically increased when an extended Na surface is introduced. The very high number of electrons in such an extended system corresponds to a dense set of KS-orbitals. In addition, the electronic states form energy-bands instead of discrete energy-levels, which adds to the complexity.

On the whole, however the picture from the Na+Cl dimer case still holds. The transfer of an electron from the Na surface to the empty $3p^6$ of the neutral Cl atom makes the ground state ionic. Contrary to the Na+Cl dimer case, this process happens at any atom-surface separation, due to the low workfunction ("ionization energy") of the extended Na(100) surface compared to that for a single Na atom. The difference between the workfunction of the Na(100) surface and the electron affinity of the Cl atom is negative (~ -1.3 eV), making the ground-state configuration ionic for all atom-surface separations ($d_{\mathrm{Cl-Na(100)}}$). Figure 5a shows the calculated ionic (adiabatic) and covalent (diabatic) PES's for the Cl/Na(100) system at different atom-surface separations. The diabatic state is purely repulsive in the Franck-Condon region of the ionic ground state. The repulsion is a result of the short-range electronic kinetic-energy (Pauli) repulsion. As a comparison, calculations on different charge configurations of the Cl atom using a jellium description of the Na surface is shown.[58]

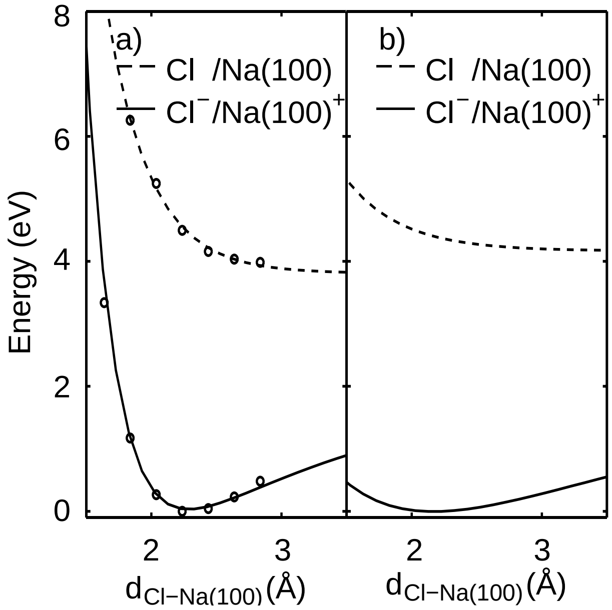

FIG. 5. The diabatic PES's for the ionic $\mathrm{Cl^-/Na(100)^+}$ ground-state (solid line) and the neutral Cl/Na(100) excited state (dashed line), as functions of the separation between the adsorbate and the surface $\mathrm{d_{Cl-Na(100)}}$ from (a) DFT calculations, and (b) jellium calculations.[58]

Figure 6 shows the calculated charge density difference between the ionic $\mathrm{Cl^-/Na(100)^+}$ ground-state and the neutral Cl/Na(100) excited state and its profile along the axis perpendicular to the surface and through the adsorbate is plotted in two parts: (a) shows the depletion in the charge density, while (b) shows the replacement of the depleted charge due to the e-h excitation introduced in the system. As seen in Fig. 6a the depletion of charge is concentrated to the Cl atom along the perpendicular axis from the surface, indicating the removal of an ionic bond and corresponds to the emptying of the $3p^6$ orbital of the Cl atom. In Fig. 6b the charge is placed in such a way that the Cl atom retrieves a spherical charge density and there is also a back-donation of charge to the Na surface. In this way the Na surface charge density gets a smooth profile with very little lateral variations in agreement with its normal Jellium appearance.

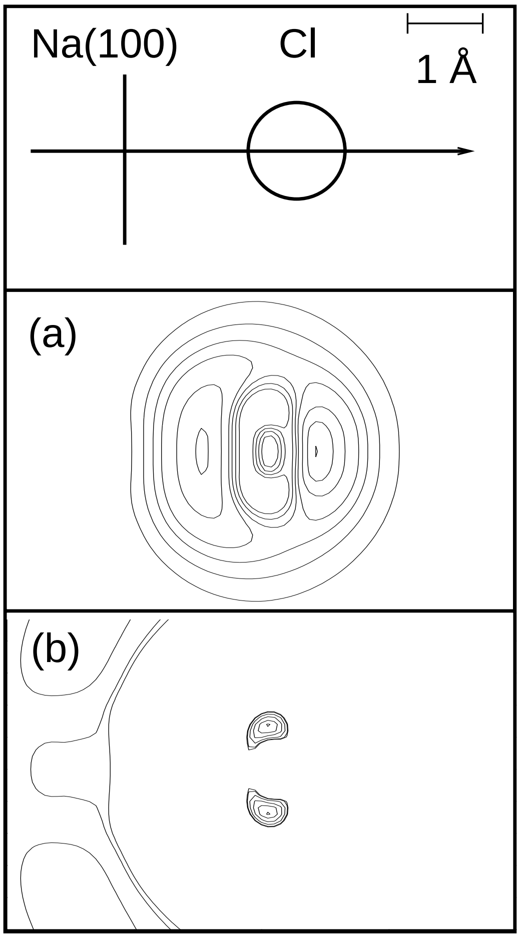

FIG. 6. The calculated charge-density difference between the ionic $\mathrm{Cl^-/Na(100)^+}$ ground-state and the neutral Cl/Na(100) excited state: (a) the depletion in the charge density, while (b) the replacement of the depleted charge due to the e-h excitation introduced in the system.

D. Cl$_2$ on the Na(100) surface

Calculation of the diabatic states for the $\mathrm{Cl_2}$ molecule in the vicinity of the Na(001) surface requires knowledge about the molecular orbitals (MO) of the free $\mathrm{Cl_2}$ molecule, which simply is a combination of atomic orbitals into MOs that suit the symmetry and lower the total energy of the molecule leaving only the $5\sigma^*(2p_z)^2$ doubly empty. In the vicinity of the Na(100) surface, there is a possibility of charge transfer of up to two electrons to the lowest unoccupied antibonding $5\sigma^*$ MO (LUMO) for the free $\mathrm{Cl_2}$ molecule.

As always, one of the requirements for charge transfer is that the electronic affinity of the $\mathrm{Cl_2}$ molecule is lower than the workfunction of the Na(100) surface, fitted with the image potential. Compared with the Cl atom there is an additional feature, caused by the competition between the time-scales for the charge transfer process and the nuclear motion of the molecule and affects the electronic affinity of the $\mathrm{Cl_2}$ molecule. If the charge transfer were slower than the nuclear motion of the Cl_2 molecule, the adiabatic affinity should be the correct one. This is the energy difference between the neutral and negatively charged states of the molecule at the intermolecular equilibrium distance for each state. However, very often the electronic transfer is such a fast process that the negatively charged Cl_2 molecule does not have time to relax into its equilibrium bondlength. Under such conditions the correct electronic affinity is the vertical one. This is the energy difference between the neutral and negatively charged molecule at the equilibrium bondlength for the neutral molecule.

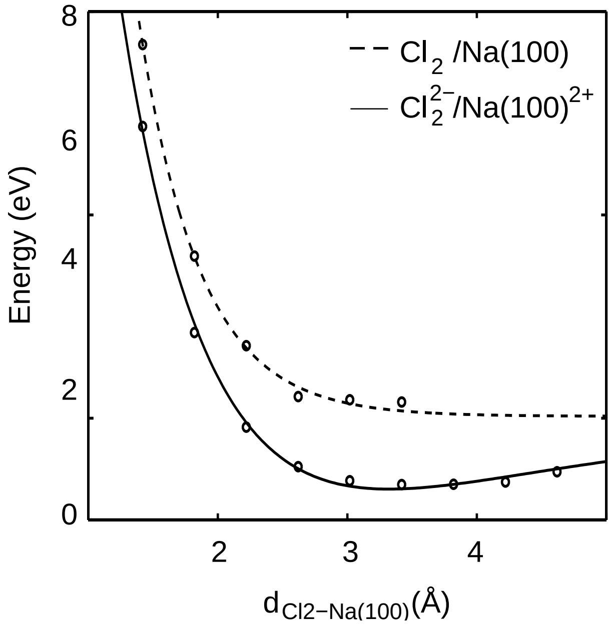

FIG. 7. The diabatic PES's for the ionic $Cl^{2-}/Na(100)^{2+}$ ground-state (solid line) and the neutral $Cl_2/Na(100)$, double e-h pair excited state, (dashed line), as a function of separation between the adsorbate and the surface $d_{Cl_2-Na(100)}$ from our DFT calculations.

Since our plan is to use the method described above in calculating diabatic PES for molecules approaching a surface in order to model, e.g., sticking behaviors, the gas-phase value of the bondlength for the Cl_2 molecule is used. The vertical affinity is estimated to lie $\sim$ 1.4 eV above the Fermi energy for the Na(100) surface[12,13]. This implies that there will be no spontaneous electronic transfer for all separations, as in the Cl/Na(100) system. However, as the neutral Cl_2 molecule approaches the surface, the image potential lowers the vertical affinity until it drops below the Fermi level and a charge transfer occurs. This is estimated to happen at around $\sim$ 10 Å from the surface[11]. The calculated LDOS's reveal that the second electron is transfered to the $5\sigma^*$ LUMO of the Cl_2 molecule for all considered molecular-surface distances.

The calculated diabatic state for the neutral Cl_2 molecule at different molecular-surface distances ($d_{Cl_2-Na(100)}$) is displayed in Figure 7. Like for the Cl/Na(100) system, the diabatic state is purely repulsive in the Franck-Condon region of the ionic ground state.

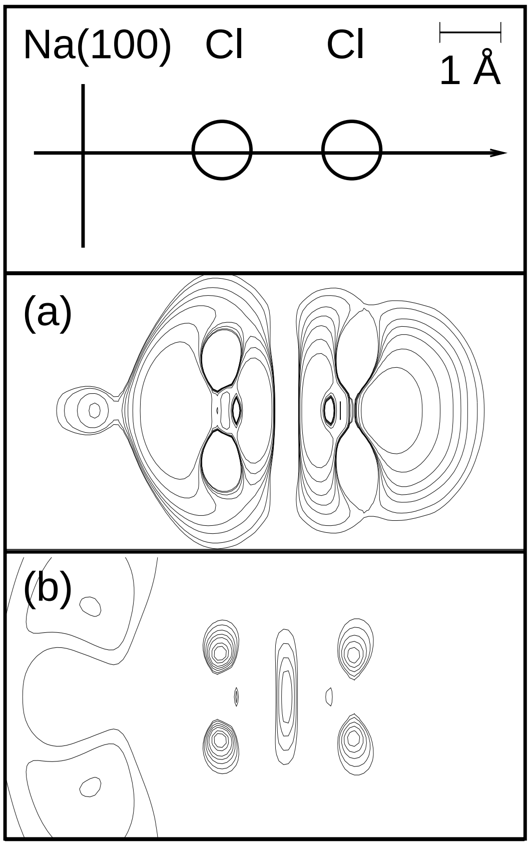

FIG. 8. The calculated charge-density difference between the ionic $Cl^{-2}/Na(100)^{+2}$ ground-state and the neutral $Cl_2/Na(100)$ double e-h pair excited state: (a) the depletion in the charge density, while (b) the replacement of the depleted charge due to the e-h excitation introduced in the system.

In Figure 8 the calculated charge density difference between the ionic $Cl^{-2}/Na(100)^{+2}$ ground-state and the neutral $Cl_2/Na(100)$ double e-h pair excited state, at the distance 3.7 Å from the surface, and its profile along the axis perpendicular to the surface and through the adsorbate is plotted in two parts: (a) shows the depletion in the charge density, while (b) shows the replacement of the depleted charge due to the e-h excitation introduced in the system. As seen in Figure 8a the charge is depleted primarily at the end of the Cl_2 molecule closest to the Na surface. There is also a depletion of the charge in the adsorption site on the Na surface. In the ground-state ionic $Cl^{-2}/Na(100)^{+2}$ system this charge indicates that the charge density around the locally positive adsorption cite relax the surrounding charge. There is also charge removed from the Cl atom that is furthest from the surface. In Figure 8b some of the removed charge is placed in the Cl_2 molecule, and gives it molecular character in the excited state instead of its ionic character in the ground-state. Most of the charge is placed in the Na surface, indicating a back-donation of charge, in agreement with the emptying of two electrons from the $5\sigma^*$ orbital of the Cl_2 molecule. In this way the Na surface charge density gets a smooth profile with very little lateral variations in agreement with its normal jellium appearance. There is also a small indication of a covalent bond between the Na surface and the neutral Cl_2 molecule.

V. RESULTS AND DISCUSSION

In this paper a simple and physically intuitive method within DFT is introduced to account for diabatic states from first-principles. Diabatic PES's are calculated and interpreted for a set of test systems with increasing complexity for pedagogical reasons. When, comparison is possible, the agreement is good between our calculated PES's and those of other calculations and experiments. This gives confidence in applying this method to other gas-surface systems in general and the O_2/Al(111) system in particular. In the latter system the diabatic PES's are essential to account for the measured sticking behavior in a diabatic charge-transfer model.[18]

Our method is a generalization of the ΔSCF method, employing DFT instead of Hartree-Fock theory. The main ideas are the creation of one or more e-h pairs and the self-consistent calculations of the modified KS system. Computationally the calculations of electronically excited states with our DFT-adapted ΔSCF-method is not much more demanding than an ordinary ground-state DFT calculation. This makes it applicable to much more complicated systems. The price to pay, however, is that the identification of relevant e-h pairs is not that obvious for extended systems. A thorough analysis of the involved charge transfer and the relevant LDOS's should be done before the calculated diabatic PES could be claimed to be the correct one.

As our method is applied to extended systems, e.g. gas-surface systems, some minor problems are encountered. The identification of the KS-hole and the creation of e-h pairs require an accurate determination of the energy eigenvalues for the desired excitation. In extended systems the KS-orbitals are densely packed in energy and the identification of the KS-hole must be done with care. This is achieved by using a dense sampling in the LDOS. In order to have convergence in extended systems, several k-point are used to sample k-space. As discussed earlier, this causes only minor difficulties in creating the e-h pairs. Using a supercell method makes the energy levels for each k-point discrete. Hence, the same procedure that is used to identify the desired excitation in the case of a single k-point sampling, as for an isolated atom and molecule, can be applied to each k-point.

A more complicated problem, which calls for a proper treatment, is the hybridization between adsorbate- and surface states. As the adsorbate approaches the surface, its orbitals overlap with those of the substrate with hybridization as a result. Hence, the LDOS smeared out on several KS-orbitals which makes the KS-hole harder to identify, and thus introduces an uncertainty in the correct way to represent the desired excited state. In this paper all the calculations for the excited states are performed by identifying the desired KS-orbital by studying the maximal projection on that orbital. Hence, the effect of hybridization is not fully taken into account, and future investigation is needed.

Another problem is that e-h pairs can be introduced only in integer units. In gas-surface systems fractionally filled KS-orbitals are encountered for intermediate separations between the adsorbate and the surface. Here this limitation unables us to determine the excited PES's completely as a function of separation. However, when diabatic PES's are calculated, the configurations at large separations are known, and the changes at smaller separations can be monitored and followed, like for molecular correlation diagrams. In between, an interpolation is needed in the regions, where a curve crossing will take place.

Finally, a difficulty not specific for extended systems should be mentioned. The exchange-correlation functional is approximated with an ordinary ground-state GGA for both the ground- and excited states. We thus assume that the change in exchange-correlation energy is small between diabatic states and that the largest contribution to our desired excitation comes from the Coulomb part of the energy functional. The reason for this is that internal charge transfers (e-h pairs) will mostly rearrange the charge density spatially in our supercell.

Examples of application of our method includes photodissociation of the NaCl dimer. The calculated dimer PES's are very close to the corresponding ones in the literature.[57] A quantitative prediction of the energy needed in the photodissociation process can be made using our calculated PES's. This energy is 5.15 eV compared with experimental value of 5.26 eV.[59]

VI. CONCLUSIONS

A simple and intuitive DFT-based ΔSCF method is proposed to calculated excitations in an extended system. Further it is applied to different test systems with an increasing degree of complexity. For each system use is made of such concepts, as KS-holes and e-h pairs introduced into some KS-orbitals in order to get the desired excitation.

The calculated diabatic PES's for two dimer cases (H_2 and NaCl) and two gas-surface systems (Cl/Na(100) and Cl_2/Na(100)) are presented. The results agree well with those of other, more accurate calculations. This gives confidence in using the method for other extended systems, where the knowledge of diabatic PES's are essential in order to explain the dynamical behavior.

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