Ab initio group model potentials including electron correlation effects

Norge Cruz Hernández and Javier Fdez. Sanz
Departamento de Química Física, Facultad de Química, E-41012, Sevilla, Spain

(Received 3 February 2000; accepted 7 July 2000)

A method for determination of ab initio group model potentials, with the intention of describing the effects of a whole molecule or a chemical group within a density functional theory framework, is reported. The one-electron part of the Kohn–Sham equations is modified by incorporation of a Coulomb operator, which accounts for the classical electron interaction arising from the group. Exchange and correlation effects are introduced by a suitable modification of the exchange-correlation functionals. The strong orthogonality condition, usually required by the theory of separability of many electron systems, is written in terms of first order reduced density matrices. In order to check the method a group model potential for H₂O (environment) was obtained and employed in the calculation of HF···H₂O and H₂O···H₂O complexes using several functionals. Equilibrium intergroup distances and binding energies are compared with all-electron calculations.

© 2000 American Institute of Physics. [S0021-9606(00)30337-3]

I. INTRODUCTION

A winning approximation in quantum chemistry, especially involved, is the classification of electrons of a given system as active or inactive. The inactive electrons may be assumed to behave as spectators and therefore can be frozen. This idea has been successfully exploited to describe the behavior of atoms or ions to model environment effects in cluster embedded calculations, as well as for the determination of effective potentials for fragments that could be employed as saturator groups. In this sense, effective potentials for NH₃, SiH₃, COOH, and cyclopentadienyl ligand have been reported.

On the other hand, some efforts have been devoted to replace a complete molecule, or chemical group, in calculations in which the environment is described through an embedding type technique. Along this line, in 1993 Mejías and Sanz reported on the determination of ab initio group model potentials (GMPs) for the HF molecule, together with some applications. Later, Frank et al. reported on the feasibility of representing spectator molecules through effective potentials generated by a semiempirical NDDO calculation. Quite recently, Day et al. came up with a method to obtain what they called an “effective fragment potential” which makes use of a distributed multipole expansion, and which allowed them to replace water molecules by an effective potential, with excellent results.

More recently we have developed polycenter compact model potentials in which the short-range contribution was expanded as a spectral representation. Also, we reported an algorithm to solve the problem associated with rotation of the model potential.

A straightforward way to improve group model potentials would involve the incorporation of the electron correlation effects between active and frozen electrons. On a general basis, this contribution could in principle be incorporated into the density functional theory (DFT) (Refs. 17, 18) framework through a modification of the exchange-correlation term. This topic has been considered for atomic cores in several works and, in this context, one of the most widely pseudopotentials used in solid-state calculations is the so-called “ultrasoft pseudopotential” (UPP) of Vanderbilt.

As to the representation beyond atomic cores, Abarenkov et al. reported a method in which the wave function of a small cluster of Li₂Mg was computed by incorporating the exchange-correlation interaction with a neighboring group in an iterative way. More recently Carter et al. presented a new embedding technique that combines periodic-DFT methods and explicit electron-correlation procedures.

Ground-state properties of chemical groups have also been studied by means of the “freeze-and-thaw” cycle of Kohn–Sham equations with constrained electron density (KSCED) as proposed by Wesolowski and Weber. In this approach, the electron density of each fragment is kept frozen while the interaction energy is calculated using terms derived from DFT, and, in addition to the exchange correlation functional, the analytical form of the approximate kinetic energy functional is needed. Examples like the water dimer, HF–HF, HCl–HCl or HCN–HF may be found as applications to the study of the hydrogen bond.

The main goal of this paper is to model the effects of a chemical group, or the environment in cluster embedded calculation, but now within the one-particle Kohn–Sham self-consistent field (SCF-KS) framework. The starting point is the electronic separability principle proposed by McWeeny and Huzinaga but involving, in this case, the first-order reduced density matrices of the separable systems. Using the Kohn–Sham orbitals such conditions lead to an operator similar to the Vanderbilt and Phillips–Kleinman pseudo-potentials. The Coulomb interaction between electrons of a given group was handled by fitting the electronic density to a set of auxiliary Gaussian functions, according to one of the

Author to whom correspondence should be addressed. Electronic mail: sanz@cica.es
strategies of Dunlap et al.29 The article is arranged as follows. The theoretical frame is briefly overviewed in Sec. II. A new separability condition in terms of group density matrices is proposed and the way to incorporate the exchange-correlation effect coming from the environment is presented. In Sec. III some test calculations concerning the H$_2$O model potential are reported. Finally the main conclusions are summarized in Sec. IV.

II. THEORETICAL ASPECTS

In the density functional theory, the SCF Kohn–Sham (SCF-KS) equations17 have to be solved,

$$\{-\frac{1}{2} \nabla^2 + V_{c}(r) + \mu_{xc}(\rho)\} \psi_{KS}^{\dagger}(r) = \varepsilon \psi_{KS}(r).$$  (1)

The term $-\frac{1}{2} \nabla^2$ is the kinetic energy operator, $V_{c}(r)$ represents the electrostatic (or Coulomb) potential, and $\mu_{xc}(\rho)$ introduces the exchange and correlation contribution, which, in general, may be written as

$$\mu_{xc}(\rho) = \frac{\partial E_{xc}(\rho)}{\partial \rho},$$  (2)

where $E_{xc}(\rho)$ is the so-called exchange and correlation functional. In local density approximation (LDA) or in the generalized gradient approximation (GGA), it is generally written as

$$E_{xc}(\rho) = \int f_{xc}(\rho, \nabla \rho) d^3 r,$$  (3)

The total electron density $\rho$ in Eq. (1) is related to the first-order density matrix for an $N$ particles system in the form

$$\rho(r) = \int \Gamma(x, x') d\sigma,$$  (4)

where the spin–orbital notation $x = (r, \sigma)$ is used and the first-order reduced density matrix is defined as30

$$\Gamma(x, x') = N \int \ldots \int \Phi^{\dagger}(x, x_1, x_2, \ldots, x_{N-1})$$
$$\times \Phi(x', x_1, x_2, \ldots, x_{N-1}) dx_1 dx_2 \ldots d_{X_{N-1}},$$  (5)

$\Phi(x_1, x_2, \ldots, x_N)$ being the electronic wave function.

The necessary and sufficient condition for the reduced density matrix to be $N$-representable18 can be expressed as

$$\Gamma = \sum \mathcal{N}_{i} |\varphi_{i}\rangle \langle \varphi_{i}|$$  (6)

with $\varphi_{i}$ being the spin–orbitals and $0 \leq n_{i} \leq 1$. Choosing $n_{i} = 0, 1$ in Eq. (5), the total electron density may be spanned on a set of spinline single-particle orbitals, each one occupied with two electrons,

$$\rho(r) = \sum_{\text{occ}} |\psi_{i}(r)|^2.$$  (7)

Let us now assume a system constituted by two molecules or chemical groups, $A$ and $B$, weakly interacting, with $\Phi_{A}$ and $\Phi_{B}$ being the wave functions. According to the building block principle of McWeeny and Huzinaga, the total electronic wave function $\Phi$ can be written as

$$\Phi = M \hat{A}(\Phi_{A} \Phi_{B}),$$  (8)

where $M$ is a normalization factor and $\hat{A}$ is the intergroup antisymmetrizer operator. For mathematical convenience in the derivation of $ab$ _initio_ model potentials, the group wave functions are selected so as to be strongly orthogonal, i.e.,

$$\int \Phi_{A}^{\dagger}(x, i, j, \ldots) \Phi_{B}(x, k, l, \ldots) dx = 0.$$  (9)

In order to keep the same condition in terms of electron density, Eq. (9) is multiplied by

$$\Phi_{A}(2, i, j, \ldots) \Phi_{B}^{\dagger}(3, k, l, \ldots)$$
and integrated with respect to $i, j, \ldots, k, l, \ldots$. Bearing in mind the form of the reduced density matrix, Eq. (9) becomes

$$\int dx \Gamma_{A}(3, x) \Gamma_{A}(x, 2) = 0.$$  (10)

Since in Eq. (9), it is possible to write $A$ in place of $B$ and $B$ place of $A$, then the strong orthogonality condition (9) in terms of reduced density matrices may be written as

$$\Gamma_{A} \Gamma_{B} = \Gamma_{B} \Gamma_{A} = 0.$$  (11)

If this condition is fulfilled, the problem of finding the local properties of the group of interest (cluster, $A$ or $B$), in the presence of a spectator group (environment, $B$ or $A$) can be set up using the DFT formalism.

According to the definition of the density matrix given in Eq. (6), the strong orthogonality condition (11) is satisfied if

$$\langle \psi_{i, \text{clus}}^{KS} | \psi_{j, \text{env}}^{KS} \rangle = 0.$$  (12)

The total reduced density matrix in a separable system may be written as

$$\Gamma_{\text{all}} = \Gamma_{\text{clus}} + \Gamma_{\text{env}},$$  (13)

and the electron density,

$$\rho(r) = \rho_{\text{clus}}(r) + \rho_{\text{env}}(r),$$  (14)

where the electron densities $\rho_{\text{clus}}(r)$ and $\rho_{\text{env}}(r)$ are normalized to the number of electrons of the cluster ($N_{\text{clus}}$) and the environment ($N_{\text{env}}$), respectively.

Under these conditions, the cluster energy in the presence of the environment (the effective energy $E_{\text{clus}}^{\text{eff}}(\rho_{\text{clus}})$) is

$$E_{\text{clus}}^{\text{eff}}(\rho_{\text{clus}}) = E_{0}(\rho_{\text{clus}}, n_{\text{clus}})$$
$$+ E_{\text{int}}(\rho_{\text{clus}} \leftrightarrow \rho_{\text{env}}, n_{\text{clus}} \leftrightarrow n_{\text{env}} \leftrightarrow \rho_{\text{env}}, n_{\text{clus}} \leftrightarrow n_{\text{env}}).$$  (15)

The first term on the right-hand side of Eq. (15) is the isolated cluster energy, excluding all components depending on the environment. The second term is the interaction of electron density in cluster $\rho_{\text{clus}}$, with electrons and nuclei of the environment $\rho_{\text{env}}$ and $n_{\text{env}}$, respectively. This last term also includes the interaction between the cluster nuclei, $n_{\text{clus}}$, and the environment negative and positive charges, which can be
added at the end of the electronic energy calculation. Notice that following Eq. (7) the cluster electron density $\rho_{\text{clus}}$ can be written as

$$\rho_{\text{clus}}(r) = \sum_{\text{occ}} |\psi_{i,\text{clus}}^{\text{KS}}(r)|^2. \quad (16)$$

Application of the variational principle to Eq. (15), together with the condition (12) leads to the set of SCF-KS-like equations

$$\{- \frac{1}{2} \nabla^2 + V_{\text{clus}}^{\text{eff}} + V_{\text{eff}}(r) + \mu_{\text{xc}}^{\text{eff}}(\rho_{\text{clus}}, \rho_{\text{env}})\} \psi_{i,\text{clus}}^{\text{KS}}(r) = e_i \psi_{i,\text{clus}}^{\text{KS}}(r). \quad (17)$$

In this equation the third and fourth terms represent the interaction between the cluster and the environment, represented through a group model potential (KS-GMP). Analyzing these contributions, one of the central points in the present work, the third term expands as

$$V_{\text{eff}}(r) = -\sum_{i} \frac{z_i}{|r-R_i|} + \int \frac{\rho_{\text{env}}(r')}{|r-r'|} d^3 r' - \hat{P}_{\text{env}}, \quad (18)$$

where the summation represents the interaction between the cluster electrons and the environment nuclei, while the integral accounts for the electron–electron interaction between the two groups. In the present work, such an interaction has been simulated by fitting the charge density of the spectator group to a set of coefficient and Gaussian functions. The algorithm used has been one of those proposed by Dunlap et al.\textsuperscript{28} whose main point is to find the set of coefficients that minimizes the functional

$$D = \int \frac{\Delta \rho(1) \Delta \rho(2)}{r_{12}} d r_1 d r_2 \quad (19a)$$

with

$$\Delta \rho(r) = \rho_{\text{env}}^{\text{exact}}(r) - \rho_{\text{env}}(r). \quad (19b)$$

The set of Gaussian functions used here was taken from Ref. \textsuperscript{28}. Finally $\hat{P}_{\text{env}}$ is a weighted projection operator over the occupied orbitals of the spectator group that allows for restriction of the variational space to the cluster space reflecting the condition given by Eq. (11),

$$\hat{P}_{\text{env}} = a \sum_{\text{occ}} |\psi_{\text{occ,env}}^{\text{KS}}(r)|^2 \psi_{\text{occ,env}}^{\text{KS}}(r) \langle \psi_{\text{occ,env}}^{\text{KS}}(r) | \psi_{\text{occ,env}}^{\text{KS}}(r) \rangle, \quad (20)$$

where the sum runs over the occupied molecular orbitals of the environment with eigenvalues $e_{\text{occ,env}}^{\text{KS}}$. The projector factor $a$ is set to $2.31$.

Concerning the fourth term of Eq. (17), the operator $\mu_{\text{xc}}^{\text{eff}}(\rho_{\text{clus}}, \rho_{\text{env}})$ arises from the exchange-correlation component of the interaction between the two groups. It can be written as

$$\mu_{\text{xc}}^{\text{eff}} = \frac{\partial E_{\text{xc,clus}}^{\text{eff}}(\rho_{\text{clus}})}{\partial \rho_{\text{clus}}} = \mu_{\text{xc}}(\rho_{\text{clus}} + \rho_{\text{env}}), \quad (21)$$

where $E_{\text{xc,clus}}^{\text{eff}}(\rho_{\text{clus}})$ is the effective exchange-correlation energy for the cluster

$$E_{\text{xc,clus}}^{\text{eff}}(\rho_{\text{clus}}) = E_{\text{xc}}(\rho_{\text{clus}} + \rho_{\text{env}}) - E_{\text{xc}}(\rho_{\text{env}}) \quad (22)$$

If a fraction of the exact Hartree–Fock exchange is used, or in a simple Hartree–Fock calculation, the exchange operator can be simulated using a nondiagonal spectral representation.\textsuperscript{5}

Equations (21) and (22) introduce the exchange and electron correlation contribution between cluster and the surrounding system in a DFT framework. These two equations are similar to those proposed by Vanderbilt\textsuperscript{22} in the UPP formulation in order to include the correlation between core and valence electrons, although in our case the determination of $V_{\text{eff}}(r)$ does not need the use of a cutoff radius. To build $V_{\text{eff}}(r)$ we only need to know an approximate density and the occupied orbitals of the surrounding system, whatever the functional used in the cluster group is. Moreover, in contrast with the KS-CED,\textsuperscript{25,26} in our method it is not necessary to use an approximated kinetic energy functional, and the inclusion of the weighted projection operator $\hat{P}_{\text{env}}$ confers a nonlocal component to $V_{\text{eff}}(r)$ as in the UPP approach. The evaluation of Eq. (22) and the part of the SCF-KS equation related to Eq. (21) was solved using the grid of points generated by the cluster system as if it were isolated.\textsuperscript{32} These algorithms were implemented in the HONDO program.\textsuperscript{33} The integrals in the atomic basis were evaluated using the King, Dupuis, and Rys\textsuperscript{34,35} and Gauss–Hermite quadratures. For integrals concerning Eqs. (19) and (20), the recursive formulas of Obara and Saika were used.\textsuperscript{36}

### III. NUMERICAL EXAMPLES

We report in this section a few numerical applications of the procedure developed above. Among other aspects, the suitability of the KS-GMPs to simulate a water molecule in the computation of the (H$_2$O)$_2$ dimer and the HF–H$_2$O complex is explored. More extensive examples in which the method is tested in surface chemistry calculations will be reported in a forthcoming work. For the present we have centered our attention on the use of a wide variety of functionals commonly used in DFT calculations. For the exchange we have selected that of Slater,\textsuperscript{37} (SLT) as well as that proposed by Becke,\textsuperscript{38} (B88). For the correlation part we employed the functional of Lee–Yang–Parr\textsuperscript{39} (LYP), which added to SLT or B88 gives two different exchange-correlation functionals: SLYP and BLYP. The widely used hybrid three parameter functional B3LYP has also been considered.\textsuperscript{40}

To set up the procedure, a first single calculation of the isolated water molecule was carried out using each of these functionals and from the KS molecular orbitals the KS-GMP was determined. These KS-GMPs were then incorporated into the DFT calculations of the active group (H$_2$O or HF) and the interaction energy was estimated at several distances. The resulting profiles were compared with those arising from reference DFT all electron (AE) calculations carried out on the supermolecules HF·H$_2$O and H$_2$O·H$_2$O. All the calculations were performed using the standard TZP basis set.

Results for the HF·H$_2$O and H$_2$O·H$_2$O complexes are reported in Tables I and II, respectively. Starting with the HF·H$_2$O system we can see that the equilibrium intermolecular distance estimated with the KS-GMP agrees reason-
TABLE II. Optimized intergroup distances (Å) and binding energies (kcal/mol) obtained for the H2O–HF system from all electron and (KS-GMP) calculations using SLT, B88, SLYP, BLYP, and B3LYP functionals. Deviations in percent are between parentheses.

<table>
<thead>
<tr>
<th>DFT functional</th>
<th>(d)</th>
<th>Binding energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>All electron</td>
<td>KS-GMP</td>
</tr>
<tr>
<td>SLT</td>
<td>1.690</td>
<td>1.573 (6.9)</td>
</tr>
<tr>
<td>B88</td>
<td>1.936</td>
<td>1.954 (0.9)</td>
</tr>
<tr>
<td>SLYP</td>
<td>1.594</td>
<td>1.540 (3.4)</td>
</tr>
<tr>
<td>BLYP</td>
<td>1.786</td>
<td>1.822 (2)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>1.763</td>
<td>1.849 (4.9)</td>
</tr>
</tbody>
</table>

The binding energies are underestimated with respect to the BSSE corrected AE ones. The energy profiles also show a suitable behavior, and as in the HF--H2O case, the curves are found to be lower according to the underestimation of the group–group interaction.

Finally, we will comment on one of the differences between our KS-GMP and the KS-CED method reported in Ref. 25. This difference concerns the use of the projection operator defined in Eq. (20), which is not present in the KS-CED formalism. In order to show the importance of this term, a set of calculations for the HF--H2O system was carried out but now setting the projection factor at \(\alpha=0\) in Eq. (20). The profile energies thus obtained are reported in Fig. 3. As can be seen, the absence of the projector gives rise to a completely attractive system whatever the functional is. This result shows the necessity of the presence of the projection operator in our representation. The presence of such a projector comes directly from the strong orthogonality condition as expressed in Eq. (11) in terms of the first-order density matrices, and taking into account the \(N\)-representability condition leads to Eq. (12).

IV. CONCLUSIONS

In this work a method to obtain polycenter group model potentials within a DFT framework is reported. The main idea underlying this approach is to carry out the calculation of an active subsystem (cluster) taking into account the influence of the surrounding groups (environment) through an \textit{ab initio} model potential, including electron correlation effects in the cluster–environment interaction. With this pur-
Pose in mind, two main modifications are introduced into the KS equations. The first one accounts for the classical electron–electron interaction between the cluster and the environment. Such an interaction involves a new term in the one-electron part and is represented through a Coulomb operator built up by fitting the electron density of the environment to a set of Gaussian functions. The second modification involves an adequate correction to the exchange-correlation operator, depending on the functional used. The exchange-correlation effects are introduced into the KS equations by means of a grid of points defined in the cluster system. In order to preserve the strong orthogonality condition between group wave functions, as required by the building block principle, an equivalent restriction is proposed using the density matrix formalism. This allows for the definition of a projection operator similar to that used in the group model potential implementation at the Hartree–Fock level.¹⁶

The whole procedure was implemented in an all-purpose program (HONDO),³³ permitting us to compute the cluster electron density with several exchange-correlation functionals (SLT, B88, SLYP, BLYP, B3LYP) within the DFT framework. In order to test the method a group model potential for H₂O was determined and used in the calculations of H₂O···H₂O and H₂O–·H₂O complexes. Compared to all-electron DFT calculations, our results show a satisfactory behavior of the water model potentials.

ACKNOWLEDGMENTS

This work was financially supported by the DGES and by the Junta de Andalucía (Spain, Projects Nos. PB98-1125 and FQM132). We are grateful to Dr. A. Márquez for his help with the HONDO implementation.