Ab initio group model potentials including electron correlation effects

Norge Cruz Hernández, and Javier Fdez. Sanz

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

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 H_2O (*environment*) was obtained and employed in the calculation of $HF \cdot \cdot \cdot H_2O$ and $H_2O \cdot \cdot \cdot H_2O$ 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 helpful in reducing the huge computational effort usually involved, is the classification of electrons of a given system as active or inactive.[1–4] 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,[5,6,7] as well as for the determination of effective potentials for fragments that could be employed as saturator groups. In this sense, effective potentials for NH_3,[8] SiH_3,[9] $COOH$,[10] and cyclopentadienyl ligand[11] 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[12] reported on the determination of *ab initio* group model potentials (GMPs) for the HF molecule, together with some applications. Later, Frank *et al.*[13] reported on the feasibility of representing spectator molecules through effective potentials generated by a semiempirical NDDO calculation. Quite recently, Day *et al.*[14] 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.[15] 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.[16]

A straightforward way to improve group model potentials would involve the incorporation of the electron correlation effects between active and frozen electrons. On a gen-

eral 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[19,20,21] and, in this context, one of the most widely pseudopotentials used in solid-state calculations is the so-called "ultrasoft pseudopotential" (UPP) of Vanderbilt.[22]

As to the representation beyond atomic cores, Abarenkov *et al.*[23] reported a method in which the wave function of a small cluster of Li_2Mg was computed by incorporating the exchange-correlation interaction with a neighboring group in an iterative way. More recently Carter *et al.*[24] 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.[25] 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.[26]

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[1] and Huzinaga[2–4] 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[22] and Phillips–Kleinman[27] 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,[28] according to one of the

a)Author to whom correspondence should be addressed. Electronic mail: sanz@cica.es

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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_2O 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) equations[17] have to be solved,

$$\{-\tfrac{1}{2}\nabla^2 + V_c(r) + \mu_{xc}(\rho)\}\psi_i^{KS}(r) = \varepsilon_i\psi_I^{KS}(r). \tag{1}$$

The term $-\tfrac{1}{2}\nabla^2$ 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

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

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

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

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

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

where the spin–orbital notation $x = (r\sigma)$ is used and the first-order reduced density matrix is defined as[30]

$$\Gamma(x,x') = N \int \int \cdots \int \Phi^*(x,x_1,x_2,\ldots,x_{N-1})$$
$$\times \Phi(x',x_1,x_2,\ldots,x_{N-1})dx_1dx_2\cdots dx_{N-1}, \tag{5}$$

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

The necessary and sufficient condition for the reduced density matrix to be N-representable[18] can be expressed as

$$\hat{\Gamma} = \sum_i n_i|\varphi_i\rangle\langle\varphi_i| \tag{6}$$

with φ_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 spinless single-particle orbitals, each one occupied with two electrons,

$$\rho(r) = \sum_{occ} |\psi_i(r)|^2. \tag{7}$$

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

$$\Phi = M\hat{A}(\Phi_A\Phi_B), \tag{8}$$

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,[1] i.e.,

$$\int \Phi_A^*(x,i,j,\ldots)\Phi_B(x,k,l,\ldots)dx = 0. \tag{9}$$

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

$$\Phi_A(2,i,j,\ldots)\Phi_B^*(3,k,l,\ldots)$$

and integrated with respect to $i,j,..,k,l,\ldots$. Bearing in mind the form of the reduced density matrix, Eq. (9) becomes

$$\int dx\Gamma_B(3,x)\Gamma_A(x,2) = 0. \tag{10}$$

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

$$\hat{\Gamma}_A\hat{\Gamma}_B = \hat{\Gamma}_B\hat{\Gamma}_A = 0. \tag{11}$$

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

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

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

$$\hat{\Gamma}_{\text{all}} = \hat{\Gamma}_{\text{clus}} + \hat{\Gamma}_{\text{env}}, \tag{13}$$

and the electron density,

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

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

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

$$E_{\text{clus}}^{\text{eff}}(\rho_{\text{clus}})$$
$$= E_0(\rho_{\text{clus}}, n_{\text{clus}})$$
$$+ E_{\text{int}}(\rho_{\text{clus}} \Leftrightarrow \rho_{\text{env}}, \rho_{\text{clus}} \Leftrightarrow n_{\text{env}}, n_{\text{clus}} \Leftrightarrow \rho_{\text{env}}, n_{\text{clus}} \Leftrightarrow n_{\text{env}}). \tag{15}$$

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 ρ_{clus}, with electrons and nuclei of the environment ρ_{env} and n_{env}, respectively. This last term also includes the interaction between the cluster nuclei, n_{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 ρ_{clus} can be written as

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

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

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

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

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

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.[29] whose main point is to find the set of coefficients that minimizes the functional

$$D = \int \frac{\Delta\rho(1)\Delta\rho(2)}{r_{12}} dr_1 dr_2 \quad (19a)$$

with

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

The set of Gaussian functions used here was taken from Ref. 28. Finally $\hat{P}_{env}$ 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),

$$\hat{P}_{env} = \alpha \sum_{occ} |\psi_{occ,env}^{KS}\rangle \varepsilon_{occ,env}^{KS} \langle \psi_{occ,env}^{KS}|, \quad (20)$$

where the sum runs over the occupied molecular orbitals of the environment with eigenvalues $\varepsilon_{occ,env}^{KS}$. The projector factor α is set to 2.[31]

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

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

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

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

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.[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[22] in the UPP formulation in order to include the correlation between core and valence electrons, although in our case the determination of the $V_{eff}(r)$ does not need the use of a cutoff radius. To build $V_{eff}(r)$ 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 KSCED,[25,26] in our method it is not necessary to use an approximated kinetic energy functional, and the inclusion of the weighted projection operator $\hat{P}_{env}$ confers a nonlocal component to $V_{eff}(r)$ 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.[32] These algorithms were implemented in the HONDO program.[33] The integrals in the atomic basis were evaluated using the King, Dupuis, and Rys[34,35] and Gauss–Hermite quadratures. For integrals concerning Eqs. (19) and (20), the recursive formulas of Obara and Saika were used.[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 $(H_2O)_2$ dimer and the HF–H_2O 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,[37] (SLT) as well as that proposed by Becke,[38] (B88). For the correlation part we employed the functional of Lee–Yang–Parr[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.[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_2O 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$\cdots H_2O$ and $H_2O\cdots H_2O$. All the calculations were performed using the standard TZP basis set.

Results for the HF$\cdots H_2O$ and $H_2O\cdots H_2O$ complexes are reported in Tables I and II, respectively. Starting with the HF$\cdots H_2O$ system we can see that the equilibrium intermolecular distance estimated with the KS-GMP agrees reason-

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TABLE I. Optimized intergroup distances (Å) and binding energies (kcal/mol) obtained for the H_2O–HF system from all electron and (KS-GMP) calculations using SLT, B88, SLYP, BLYP, and B3LYP functionals. Deviations in percent are between parentheses.

| DFT functional | d | | Binding energy | | |
	All electron	KS-GMP	All electron	KS-GMP	E_{cor}
SLT	1.690	1.573 (6.9)	−13.2	−11.2 (3.4)	−11.6
B88	1.936	1.954 (0.9)	−6.6	−4.7 (14.5)	−5.5
SLYP	1.594	1.540 (3.4)	−17.5	−15.1 (3.8)	−15.7
BLYP	1.786	1.822 (2)	−9.6	−6.8 (18)	−8.3
B3LYP	1.763	1.849 (4.9)	−10.1	−7.2 (20)	−9.0

ably with those obtained from AE calculations. With the exception of SLT based functionals, the KS-GMP distances are found to be larger than the AE ones, the errors ranging between 0.9% and 6.9%. The KS-GMP binding energies computed at the optimized intermolecular distances appear to be significantly lower than the AE ones; however, it should be noted that the AE binding energies are overestimated because of the basis set superposition error (BSSE). Since the KS-GMP are free of BSSE, we corrected the AE energies using the well-known counterpoise method of Boys and Bernaldi.[41] These corrected energies are also reported in the table under E_{cor} entry. As can be seen, the agreement is clearly improved, with deviations between 3% and 20%. The observed general trend is an underestimation of the binding energies reflecting the fact that the model potential is frozen and, therefore, no repolarization of the electron distribution is allowed. Also, because no basis set is present in the GMP, the electron density and, therefore, the intergroup region are not properly described. An additional approximation introduced in the KS-GMP calculations arises from the way of computing the energy and integrals related to Eq. (21, 22), where only the grid generated by the cluster is used. Finally, in Fig. 1, the profile energies obtained from KS-GMP and AE calculations are plotted. It shows that beyond the numerical reasonable agreement, the shape of these curves appears to be quite satisfactory, with smooth behavior and a suitable description of the equilibrium region.

Results obtained for the $H_2O\cdots H_2O$ dimer are reported in Table II and Fig. 2. Both intergroup and binding energies are found to follow the trends already mentioned above. The equilibrium distances appear to be overestimated (10%–14%) again with the exception of the SLT functionals, while

TABLE II. Optimized intergroup distances (Å) and binding energies (kcal/mol) obtained for the H_2O–H_2O system from all electron and (KS-GMP) calculations using SLT, B88, SLYP, BLYP, and B3LYP functionals. Deviations in percent are between parentheses.

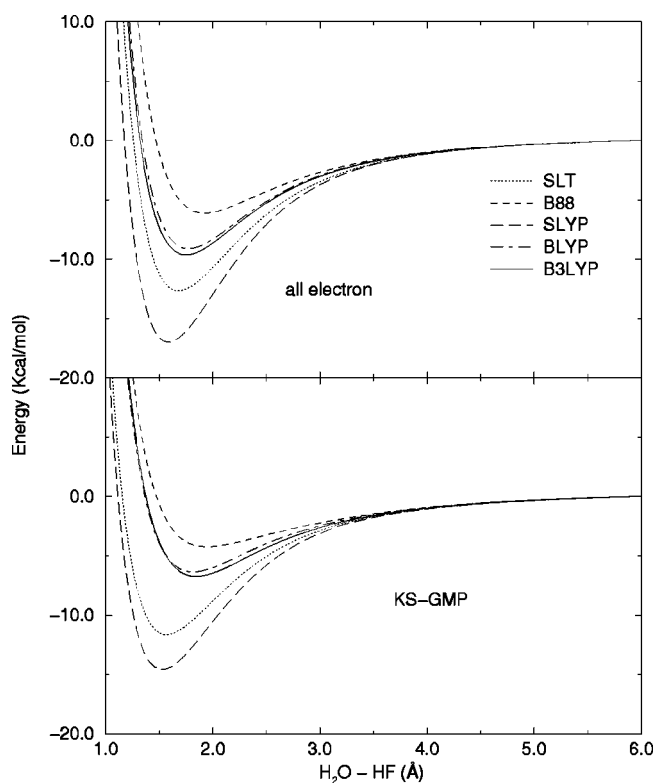| DFT functional | d | | Binding energy | | |
	All electron	KS-GMP	All electron	KS-GMP	E_{cor}
SLT	1.839	1.785 (2.9)	−8.4	−6.5 (6.1)	−6.9
B88	2.200	2.576 (14.6)	−3.2	−1.9 (24.9)	−2.5
SLYP	1.719	1.708 (0.6)	−11.8	−8.9 (15.3)	−10.5
BLYP	1.976	2.192 (10.9)	−5.3	−3.5 (22.2)	−4.5
B3LYP	1.953	2.182 (11.7)	−5.7	−3.8 (22.4)	−4.9

FIG. 1. Binding energy profiles for the H_2O–HF complex from all-electron and KS-GMP calculations.

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$\cdots H_2O$ case, the curvatures 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 KSCED method reported in Ref. 25. This difference concerns the use of the projection operator defined in Eq. (20), which is not present in the KSCED formalism. In order to show the importance of this term, a set of calculations for the HF$\cdots H_2O$ 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 *ab initio* model potential, including electron correlation effects in the cluster–environment interaction. With this pur-
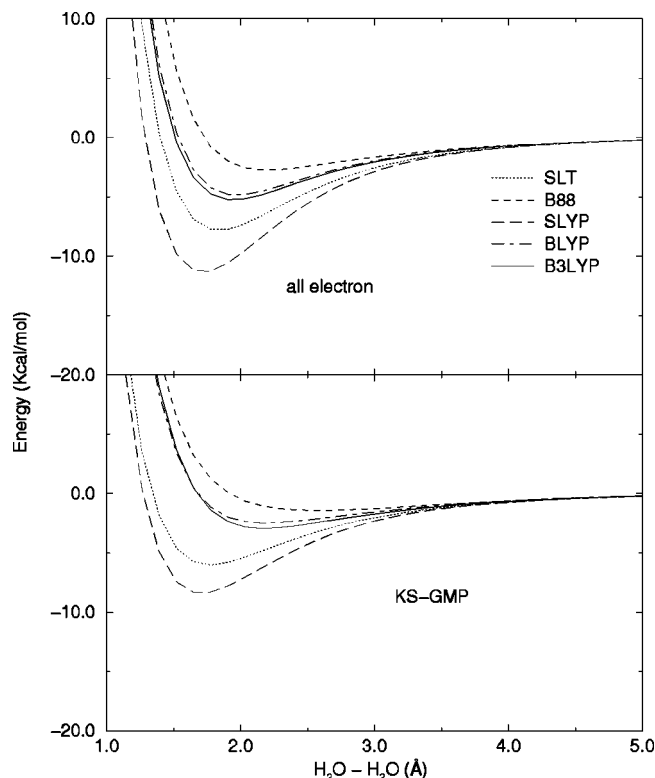
FIG. 2. Binding energy profiles for the $H_2O–H_2O$ dimer from all electron and KS-GMP calculations.

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 group 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
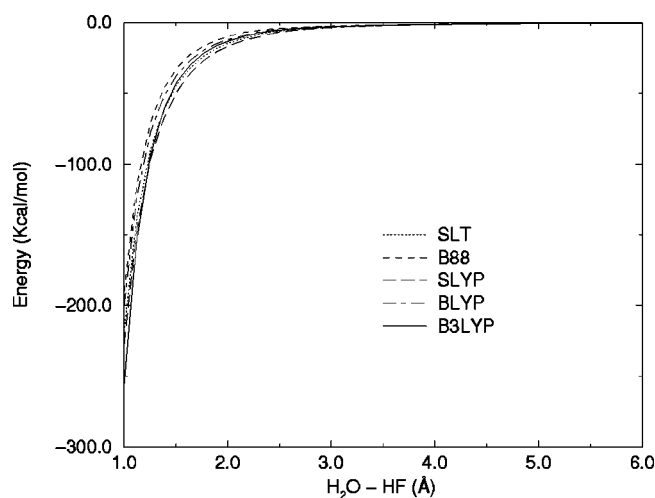
system. In order to preserve the strong orthogonality condition between group wave functions, as required by the building block principle, an equivalent restriction is proposed using the density matrix formalism. This allows for the definition of a projection operator similar to that used in the group 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 H_2O was determined and used in the calculations of $HF\cdots H_2O$ and $H_2O\cdots H_2O$ complexes. Compared to all-electron DFT calculations, our results show a satisfactory behavior of the water model potentials.

ACKNOWLEDGMENTS

FIG. 3. Binding energy profiles for the $H_2O–HF$ complex computed without the projector operator in the KS-GMP.

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