Test of a bond-pair superposition model describing the interaction between atoms: Application to the hydrides of the first-row elements

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The performance of a recently proposed *ab initio* description of chemisorption problems, obtained by reducing the total many-body Hamiltonian to a superposition of bond-pair Hamiltonians, is tested. This scheme, which in its Hartree-Fock version leads to an independent-particle model of the tight-binding form, is applied to analyze the interaction curves for the hydrides of the first-row elements as a function of internuclear distances. By fixing the occupation numbers for the orthonormal spin orbitals at large internuclear separations, its relationship with results from both the valence-bond and the molecular-orbital methods is established. It is shown that the model works fairly well in predicting binding energies, equilibrium distances, dipole moments, and vibrational frequencies for the whole series of the hydrides. It was also found that if a consistent expansion of the intervening parameters is made up to second order in the atomic-orbital overlaps, reasonable results are obtained for the hydrides forming bonds of nearly ionic character: LiH, OH, and FH.

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I. INTRODUCTION

The use of tight-binding (TB) or linear combination of atomic orbitals methods is gaining increasing attention in applications to a wide variety of problems in solid-state physics. Its computational simplicity makes these methods very attractive in dealing with periodic or non-periodic systems where alternative methods require sophisticated programming and sometimes prohibitively long computing times.

In particular, with regard to chemisorption problems a great deal of progress has been achieved through elaborate numerical calculations based on the local-density approximation (LDA) [1,2]. This approach has been successfully applied to atoms adsorbed on metals or semiconductor surfaces and only to very simple cases of chemisorbed molecules.

In the context of more complicated chemisorption systems or other problems of nonperiodic nature, it is highly desirable to have a TB approach which may offer an alternative to LDA calculations. Conventionally TB is a semiempirical method in which the parameters entering the Hamiltonian are determined from bulk band-structure data. However, it is clear that seeking a TB scheme able to compete with LDA should be attempted without relying on the use of semiempirical or adjustable parameters. Several theoretical efforts have been devoted to putting this method on a more fundamental basis, mainly on the grounds of the stationary properties of the self-consistent solutions of the density-functional theory. Liu *et al.* [3] presented a TB method based on a superposition of dimers treated within the LDA scheme, which does not require arbitrary parameters, and applied it to the calculation of the electronic structure for transition-metal elements. It is also in this direction that Goldberg

et al. [4] and García Vidal *et al.* [5] have recently developed an approximate method in which an *ab initio* procedure is proposed to obtain the TB parameters without the use of adjustable "constants."

The basic idea is to construct an effective Hamiltonian which can be considered a superposition of Hamiltonians defined for each pair of bonds. Starting with a many-body Hamiltonian written in terms of an orthonormal basis, only those terms leading to bond-pair interactions are retained. The resulting many-body Hamiltonian treated within a Hartree-Fock (H-F) approximation [4] leads to a TB form, with parameters given in terms of one- and two-electron integrals as well as certain averages of fermionic creation and annihilation operators corresponding to the orthonormal states. It is also possible to go beyond the HF approximation by including electronic correlations as in the LDA [5]. Under these schemes only a few examples were examined: He on metals [4], H on Al and Li [5], and the early stages of the interface formation in K-GaAs(110) [6,7].

In order to test the capabilities of this model and aiming to future applications to complex chemisorption systems as well as to dynamical problems such as scattering and sputtering processes, a systematic analysis of its HF version, when applied to diatomic systems containing hydrogen, is presented in this paper. The importance of including spin-flip terms in the Hamiltonian, which were absent in [4] and [5], is also examined. We also consider the approximation in which the TB parameters are expanded up to second order in the atomic-orbital overlaps, with particular attention to keeping the whole expansion consistent up to this order.

In Sec. II a brief description of the model and the calculation procedure are given. Numerical results and discussion are presented in Sec. III. Section IV is devoted to concluding remarks.

II. THEORY

A. Model Hamiltonian

As a first stage, the many-body Hamiltonian for a system of interacting atoms written in a second-quantized language is approximated as

$$\hat{H} = \sum_{i,\sigma} \varepsilon_i \hat{n}_{i\sigma}$$

$$+ \frac{1}{2} \sum_{i,\sigma} \left[U_i \hat{n}_{i-\sigma} + \sum_{j(\neq i)} J_{ij} \hat{n}_{j-\sigma} + \sum_{j(\neq i)} G_{ij} \hat{n}_{j\sigma} \right] \hat{n}_{i\sigma}$$

$$+ \sum_{i \neq j, \sigma} (\hat{T}_{ij}^\sigma + \tfrac{1}{2} J_{ij}^x c_{j-\sigma}^\dagger c_{i-\sigma}) c_{i\sigma}^\dagger c_{j\sigma}$$

$$+ \frac{1}{2} \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} . \tag{1}$$

The index i denotes the orthonormal atomic basis set $\{\phi_i\}$ and $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ is the fermionic number operator. The last term in Eq. (1) corresponds to the repulsion between nuclei of charges Z_α, Z_β. Equation (1), to be referred as MH-ORTH, an abbreviation of model Hamiltonian–orthonormal, is obtained from the general form of the Hamiltonian by neglecting all terms involving four different spin orbitals, except those spin-flip terms of type $c_{j-\sigma}^\dagger c_{i-\sigma} c_{i\sigma}^\dagger c_{j\sigma}$. The result of this approximation is a many-body Hamiltonian written as a superposition of bond pairs. It is worth noting that if we were dealing with a hydrogen molecule involving only states a and b obtained from two mutually orthogonalized $1s$ H orbitals, the approximation in Eq. (1) amounts to ignoring terms of the form $a_\sigma^\dagger b_\sigma a_{-\sigma}^\dagger b_{-\sigma}$. These correspond to a transference of two paired electrons from state b to a and vice versa. The parameters and the operator $\hat{T}_{ij}^\sigma$ in Eq. (1) are given by (in a.u.),

$$t_{ij} = \left\langle \phi_i(\mathbf{r}) \left| -\frac{1}{2}\nabla_r^2 - \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|} \right| \phi_j(\mathbf{r}) \right\rangle ,$$

$$\varepsilon_i = t_{ii} \tag{2a}$$

$$h_{k,ij} = \left\langle \phi_k(\mathbf{r})\phi_i(\mathbf{r}') \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \phi_k(\mathbf{r})\phi_j(\mathbf{r}') \right\rangle ,$$

$$J_{ij} = h_{i,jj} , \quad U_i = h_{i,ii} \tag{2b}$$

$$h_{k,ij}^x = \left\langle \phi_k(\mathbf{r})\phi_i(\mathbf{r}') \left| \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right| \phi_j(\mathbf{r})\phi_k(\mathbf{r}') \right\rangle ,$$

$$J_{ij}^x = h_{i,jj}^x \tag{2c}$$

$$G_{ij} = J_{ij} - J_{ij}^x , \tag{2d}$$

$$\hat{T}_{ij}^\sigma = t_{ij} + \sum_k h_{k,ij}\hat{n}_{k-\sigma} + \sum_k (h_{k,ij} - h_{k,ij}^x)\hat{n}_{k\sigma} , \tag{2e}$$

where $\mathbf{r}$ and $\mathbf{R}$ denote electronic and nuclear coordinates, respectively.

The orthonormal basis set $\{\phi_i\}$ is assumed to be constructed according to the symmetric orthogonalization procedure [8]:

$$\phi_i = \sum_j (1+S)_{ij}^{-1/2} \psi_j , \tag{3}$$

where ψ_j represents an atomic orbital (j labels the type of orbital and the atom site) and S_{ij} are the corresponding overlap matrix elements. By expanding Eq. (3) up to second order in the overlap S, replacing in Eqs. (2), and retaining only those terms which maintain the Hamiltonian as a superposition of bond pairs, we arrive at an expression completely equivalent to Eq. (1):

$$\hat{H} = \sum_{i,\sigma} \hat{\tilde{E}}_{i\sigma}\hat{n}_{i\sigma}$$

$$+ \frac{1}{2}\sum_{i,\sigma} \left[\tilde{U}_i \hat{n}_{i-\sigma} + \sum_{j(\neq i)} \tilde{J}_{ij}\hat{n}_{j-\sigma} + \sum_{j(\neq i)} \tilde{G}_{ij}\hat{n}_{j\sigma} \right] \hat{n}_{i\sigma}$$

$$+ \sum_{i \neq j, \sigma} (\hat{\tilde{T}}_{ij}^\sigma + \tfrac{1}{2}\tilde{J}_{ij}^x c_{j-\sigma}^\dagger c_{i-\sigma}) c_{i\sigma}^\dagger c_{j\sigma}$$

$$+ \frac{1}{2}\sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \tag{4}$$

with parameters redefined as

$$\hat{\tilde{E}}_{i\sigma} = \varepsilon_i^0 - \sum_j S_{ij}\hat{T}_{ij}^\sigma + \tfrac{1}{4}\sum_j S_{ij}^2 \left[\left[\varepsilon_i^0 + \sum_k J_{ik}^0 \hat{n}_{k-\sigma} + \sum_{k(\neq i \neq j)} (J_{ik}^0 - J_{ik}^{x0})\hat{n}_{k\sigma} \right] - \left[\varepsilon_j^0 + \sum_k J_{jk}^0 \hat{n}_{k-\sigma} + \sum_{k(\neq i \neq j)} (J_{jk}^0 - J_{jk}^{x0})\hat{n}_{k\sigma} \right] \right] \tag{5a}$$

and

$$\tilde{U}_i = U_i^0 - \sum_j S_{ij}^2 J_{ij}^{x0} , \tag{5b}$$

$$\tilde{J}_{ij} = J_{ij}^0 - S_{ij}^2 J_{ij}^{x0} , \tag{5c}$$

$$\tilde{G}_{ij} = (J_{ij}^0 - J_{ij}^{x0})(1 + S_{ij}^2) , \tag{5d}$$

$$\tilde{J}_{ij}^x = J_{ij}^{x0} - \sum_k (S_{ik}h_{jik}^{x0} + S_{jk}h_{ijk}^{x0}) + \sum_k (S_{jk}^2 J_{ik}^{x0} + S_{ik}^2 J_{jk}^{x0})$$

$$+ \tfrac{3}{4}\sum_k (S_{ik}^2 J_{ij}^{x0} + S_{jk}^2 J_{ij}^{x0}) + \tfrac{1}{2}S_{ij}^2(J_{ij}^{x0} + J_{ij}^0) . \tag{5e}$$

In Eqs. (5a)–(5e) the parameters with a superscript 0 correspond to expressions (2) obtained by replacing the orthonormal states by the atomic orbitals. The hopping operator $\hat{T}$ is kept in the orthonormal basis according to Eq. (2e), having, in this form, the possibility of being associated with Bardeen's tunneling current [4].

It is important to note that the success of this kind of model rests on a delicate balance among the different interactions retained. Thus one has to be sure that all approximate terms entering the Hamiltonian have been consistently expanded up to the same order. We found that a consistent expansion of the model Hamiltonian up

to second order in the atomic overlaps (hereinafter referred to as MH-S2) within the conception of bond-pair superposition and requires the Coulomb interaction parameters in Eqs. (5b)–(5d) to be corrected through the $S^2 J^{x0}$ terms. These corrections have not been taken into account in previous works [4–7]. We have also retained the spin-flip contributions expanded up to second order to ensure the consistency of the MH-S2 model.

B. Calculation procedure

The calculation for the hydrides of the first-row elements was performed within an all-electron self-consistent HF scheme, using the model Hamiltonian corresponding to MH-ORTH and MH-S2 according to Eqs. (1) and (4), respectively. The main points on which the computation is based are the following.

1. The self-consistent procedure

The ground state is taken as a single Slater determinant $|\Phi\rangle$ constructed by occupying with N electrons the lowest-energy one-electron molecular orbitals (MOs) $\{\varphi_\alpha^\sigma\}$. These MOs are assumed to be expanded in an orthonormal atomic basis $\{\phi_i\}$ and consequently the density matrix elements are given by

$$\varphi_\alpha^\sigma = \sum_i c_i^{\alpha\sigma} \phi_i \Longrightarrow \rho_{ij}^\sigma = \sum_{\alpha \text{ occ}} c_i^{\alpha\sigma *} c_j^{\alpha\sigma} = \langle c_{i\sigma}^\dagger c_{j\sigma} \rangle \qquad (6)$$

where $\langle c_{i\sigma}^\dagger c_{j\sigma} \rangle$ denotes the average value on the ground state $|\Phi\rangle$ of the fermionic operators creating and destroying the orthonormalized atomic states. At large internuclear distances these matrix elements are given by

$$\rho_{ij}^\sigma = \begin{cases} \delta_{ij} & \text{if } i=j \text{ corresponds an occupied atomic state} \\ 0 & \text{otherwise .} \end{cases} \qquad (7)$$

The self-consistent calculation starts with the configuration given by Eq. (7) as it follows from the application of Hund's rules to each atom. The initial point is taken as the separate atom limit for which the charge configuration is known. The spin component s_z for the molecule is selected by pairing the corresponding states of the atoms forming the dimers. This produces the initial set of MOs and also the output values of ρ_{ij}^σ. For decreasing internuclear distances, the inputs ρ_{ij}^σ are taken as the corresponding self-consistent output values of the previous point. In this form self-consistency is achieved more efficiently.

2. Total energy

In each step the total energy is calculated as

$$E_{AH} = \sum_{\substack{\alpha,\sigma \\ \text{occ}}} \varepsilon_\alpha^\sigma - [X] + \frac{Z_A Z_B}{|R_A - R_H|} , \qquad (8)$$

where $\varepsilon_\alpha^\sigma$ is the eigenvalue of the corresponding occupied MO and $[X]$ symbolizes the whole set of terms to be subtracted according with the HF approximation for the Hamiltonians in Eqs. (1) or (4).

3. Basis set

The more appropriate minimal basis set of an atom is the set of the HF atomic orbitals. These can be selected as the Clementi-Roetti [9] atomic orbitals based on the Slater-type orbitals (STOs) [10]. However, several authors favored the use of Gaussian-type orbitals (GTOs) instead of STOs for calculations involving polyatomic systems. In the present work we use the HF atomic basis set calculated in terms of GTOs given by Huzinaga [11].

4. Interaction energy

The interaction energy between atom A and H is defined as

$$E_{\text{int}}(R) = E_{AH}(R) - (E_A + E_H) . \qquad (9)$$

E_A and E_H are the total energies of the isolated atoms A and H, respectively. $E_{AH}(R)$ is the total energy when A and H are brought together at an internuclear distance R. However, if finite atomic basis sets are used to calculate
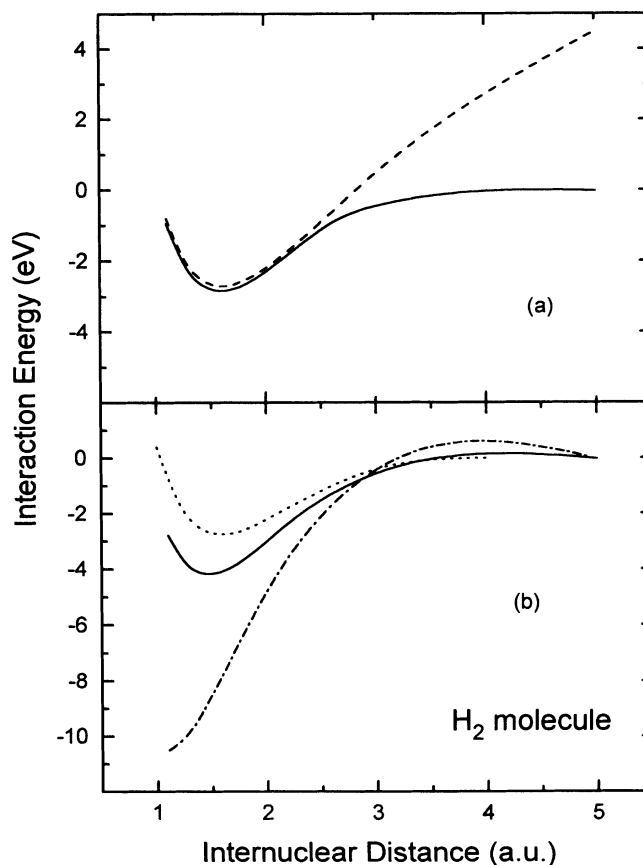

FIG. 1. The H_2 molecule. (a) ——, the MH-ORTH calculation; – – –, a complete Hamiltonian calculation. (b) The MH-S2 calculation. ——, the $S^2 J^{x0}$ renormalization and the spin-flip terms included; · · · ·, the $S^2 J^{x0}$ renormalization and the spin-flip terms both neglected; —·—·—·, the $S^2 J^{x0}$ renormalization included while the spin-flip terms are neglected.

TABLE I. Electronic energies from different methods at different internuclear distances.

Method of calculation	$R = 1.5$ a.u.	$R = 3.0$ a.u	$R \rightarrow \infty$
E^{MO}	$2\varepsilon + U/2 + J/2 + J^x + 2(t+h)$	$2\varepsilon + U/2 + J/2 + J^x + 2(t+h)$	$2\varepsilon + U/2 + J/2 + J^x + 2(t+h)$
E^{VB}	$2\varepsilon + J$	$2\varepsilon + J$	$2\varepsilon + J$
E^{MH}	$2\varepsilon + U/2 + J/2 + J^x/2 + 2(t+h)$	$2\varepsilon + 0.17U + 0.83J + 1.16(t+h)$	$2\varepsilon + J$

molecular and atomic energies, an erroneous result for E_{int} is obtained using Eq. (9) [11]. This effect can be corrected by keeping the basis sets on sites A and H, but removing the nucleus and the electrons corresponding to the atom H (A) in each case. Thus the calculation of the "atomic" energy of A (H) is performed in the presence of the "ghost atom" orbitals H (A) at a distance R [11]. The model Hamiltonian based on an orthonormal basis set provides a natural way to the ghost atom concept in the calculation of the atomic energies $E_{A(H)}(R)$. The corrected interaction energy expression is

$$E_{int}(R) = E_{AH}(R) - [E_{A(H)}(R) + E_{H(A)}(R)] ,$$

$$E_{A(H)}(\infty) + E_{H(A)}(\infty) = E_A + E_H .$$

(10)

5. Dimer characterization

The magnitudes chosen to characterize each dimer are the binding energy (E_B), the equilibrium distance (R_e), the vibrational frequency (ω_e), and the dipole moment (μ). The E_B and R_e values are obtained from the interaction energy curve, while ω_e is obtained by fitting the calculated results to a Morse potential. The dipole moment is calculated using

$$\mu = \sum_{\alpha \; occ} \langle \varphi_\alpha^\sigma | \mathbf{r} | \varphi_\alpha^\sigma \rangle = \sum_{\alpha \; occ} \sum_{i,j} a_{\alpha\sigma}^i a_{\alpha\sigma}^j \langle \phi_i | \mathbf{r} | \phi_j \rangle , \qquad (11)$$
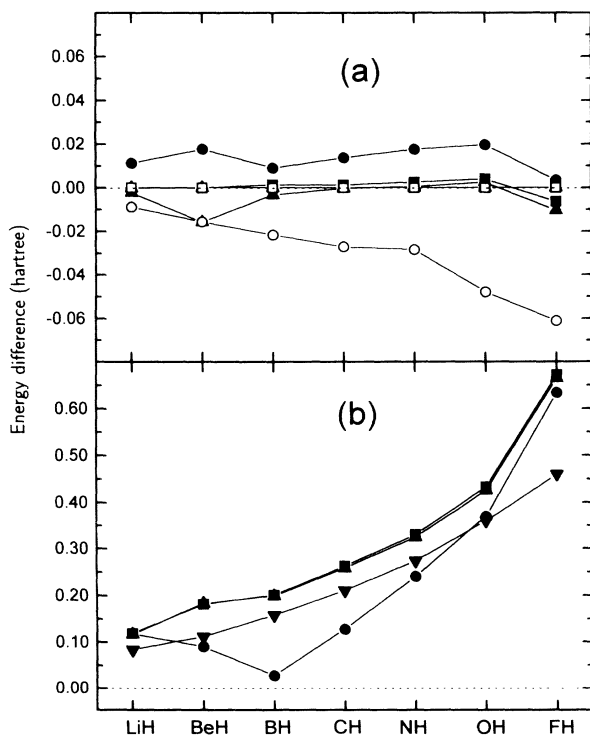

FIG. 2. (a) Differences between the atomic energy calculated in the presence of the ghost atom and the HF value for the isolated atom. ● MH-S2 calculation for A-like atom energy; ▲ MH-ORTH calculation; ■, complete Hamiltonian calculation. The empty symbols are the results for the H-atom energy. (b) Differences between the calculated total energy and the experimental value. ● MH-S2 calculation; ▲, MH-ORTH calculation; ■, complete Hamiltonian with atomic basis set; ▼, complete Hamiltonian with molecular basis set.
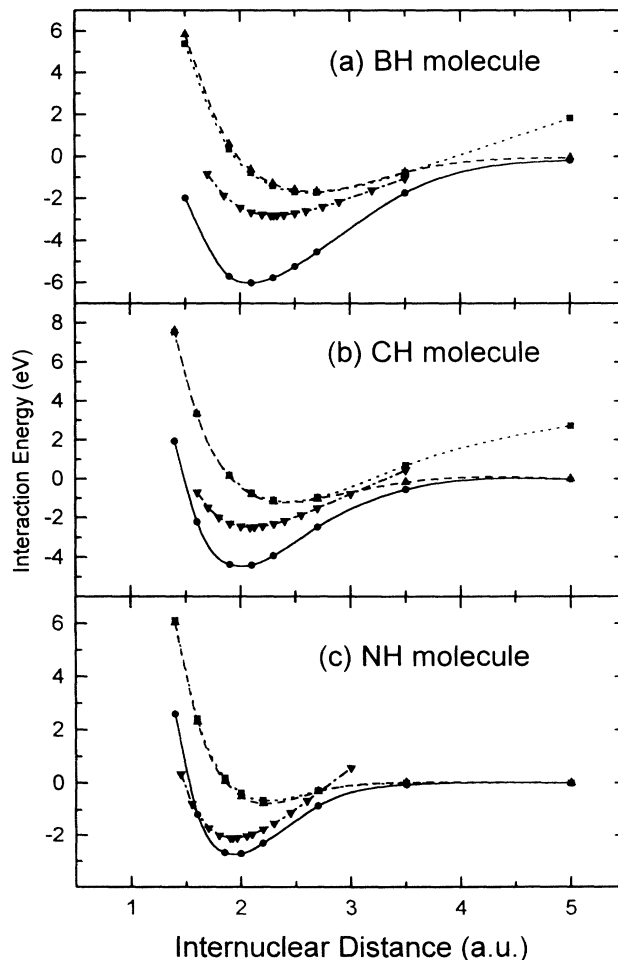

FIG. 3. Interaction energies for the (a) BH molecule, (b) CH molecule, and (c) NH molecule. The following symbols are the result for all cases: ●, MH-S2 calculation; ▲, MH-ORTH calculation; ■, complete Hamiltonian with atomic basis set; ▼, complete Hamiltonian with molecular basis set. Broken or continuous lines are guides to the eye.

where $a^i_{a\sigma}$ is the weight of the orthonormal atomic function ϕ_i in the α molecular orbital with spin $\sigma, \varphi^{\sigma}_{\alpha}$.

III. RESULTS AND DISCUSSION

Before considering hydrides, it is convenient to examine the significance of the terms neglected in Eq. (1) and the consistency effects on the expansion up to second order in the overlaps by analyzing our results for the H_2 molecule.

A. H_2 molecule

In Fig. 1(a) the results corresponding to the application of the MH-ORTH are compared with those obtained by using the complete Hamiltonian [12], both calculated with the same basis set. It can be observed that in the region where the atoms interact strongly, the results are practically the same. However, in the dissociation limit, those obtained with the complete Hamiltonian exhibit the well-known behavior of the molecular-orbital method due to the overestimation of the weight of the ionic configurations on the ground state. This does not occur in our model and the reason can be traced back to the situation selected as the starting point for doing the calculation. This selection plays an essential role in our method since it results in an unbalance in the diagonal matrix elements of the Hamiltonian, thus avoiding spurious degeneracies after diagonalization. The molecular-orbital method applied to homonuclear modules [13] assumes, based on symmetry, that similar atomic orbitals form a molecular orbital with the same weight ($|1/\sqrt{2}|$ either for the bonding or antibonding state). This gives rise to an equal occupation of the orthogonalized atomic states.

TABLE II. Dimer characterization. R_e is expressed in a.u., E_B in eV, μ in debyes, and ω_e in cm^{-1}. R_e and E_B were obtained from the calculated interaction energy curve, while ω_e from a fitting with a Morse curve.

| | | Model Hamiltonian | | | |
Hydride		ORTH	S2	Complete Hamiltonian[a]	Expt.[b]
LiH	R_e	3.0	3.0	3.0	3.015
	E_B	−0.88	−0.95	−0.86	−2.52
	μ	5.009	5.702	5.085	5.882[c]
	ω_e	664.3	576.3		1405.6
BeH	R_e	3.0	2.5	2.8	2.538
	E_B	−0.55	−3.33	−0.933	−2.6
	μ	0.994	1.542	1.208	
	ω_e	576.8	1653.3		2058.6
BH	R_e	2.7	2.1	2.6	2.336
	E_B	−1.65	−6.00	−1.71	−3.58
	μ	−0.819	−0.240	−1.536	−1.3[d]
	ω_e	907.7	2160.6		2367.5
CH	R_e	2.3	2.1	2.46	2.124
	E_B	−1.17	−4.39	−1.15	−3.65
	μ	−1.201	−0.515	−1.134	−1.46[c]
	ω_e	959.5	2347.5		2868.5
NH	R_e	2.2	2.0	2.24	1.9614
	E_B	−0.76	−2.71	−0.65	−3.80
	μ	−1.292	−0.946	−1.245	−1.3[d]
	ω_e	937.3	2140.6		3125.6
OH	R_e	2.0	2.0	2.0	1.8342
	E_B	−1.30	−2.06	−1.13	−4.63
	μ	−1.673	−0.958	−1.666	−1.66[c]
	ω_e	1258.2	1973.4		3735.2
FH	R_e	1.89	1.85	1.90	1.7328
	E_B	−2.11	−2.40	−2.56	−6.12
	μ	−1.797	−1.708	−1.811	−1.8195[c]
	ω_e	1701.6	2009.5		4139.0

[a]Reference [12].
[b]Reference [14].
[c]J. Pople and D. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).
[d]A. A. Radzig and B. M. Smirov, in *Reference Data on Atoms, Molecules and Ions*, edited by V. I. Goldanskii, R. Gomer, F. P. Schäfer, and J. P. Toennies, Series in Chemical Physics, Vol. 31 (Springer-Verlag, Berlin, 1985).

Thus the assumption that similar states on different atoms participate equally in forming the molecular orbitals precludes the localization of electrons around any particular nucleus. Although this is not serious in the regions where the atoms interact strongly, it is the source of the deficiencies of the molecular-orbital method at large internuclear separations.

In Table I we show the results for the total electronic energy in the singlet ground state obtained by using two $1s$ orthonormal states, corresponding to (i) the MO method (E^{MO}), (ii) the valence-bond method (E^{VB}), and (iii) the MH-ORTH (E^{MH}). The latter was obtained by taking the occupation numbers which result from the self-consistent procedure at each internuclear distance. It can be seen that our description behaves as the valence-bond method at $R \to \infty$, while at the equilibrium distance it approaches the MO method. The difference in $J^x/2$ with this latter scheme arises from the terms $a^\dagger_{-\sigma}b_{-\sigma}a^\dagger_\sigma b_\sigma$, which has been ignored in our treatment. It is interesting to note that at $R = 3.0$ a.u. the MO method overestimates the on-site Coulombic repulsion with reference to our model ($0.5U$ against $0.17U$) and underestimates the intersite interaction ($0.5J$ against $0.83J$). For decreasing distances the density-matrix elements at the previous point are taken as input values for the new self-consistent calculation. Thus the system "remembers" the total spin symmetry of the ground state at each point and this determines the "path" followed in searching for the energy minimum at the next point. In Fig. 1(b) we observe three interaction energy curves obtained by applying the MH-S2 model, with (a) corrections of the type $S^2 J^{x0}$ and spin-flip terms included, (b) both effects neglected, and (c) corrections $S^2 J^{x0}$ included while the spin-flip terms are ignored. It can be observed that

one arrives at a very poor description when terms of the same order of importance are not treated on an equal footing. Also it is noted that the MH-S2 description leads to a binding energy larger than that obtained from a MH-ORTH calculation.

B. Hydrides AH (A=Li, Be, B, C, N, O, and F)

In Fig. 2(a) the differences between HF atomic energies calculated with and without the presence of the ghost atom are shown. Results for the atomic energies obtained from the MH-ORTH and the MH-S2 models are compared with the results obtained from a full all-electron HF calculation. These all correspond to the theoretical equilibrium distance for the respective dimer AH. In general, the MH-S2 introduces marked changes of the "atom energy" in the molecule with reference to the isolated atom values, giving systematically an energy smaller for the A atom and larger for H in the different hydrides.

Total-energy differences with respect to the experimental values calculated with our model and the complete Hamiltonian at the theoretical equilibrium distances are shown in Fig. 2(b). The filled-inverted triangle curve shows the difference between the experimental values and the Cade-Huo results [14]. As this calculation was performed within a full all-electron self-consistent HF scheme using an atomic basis set optimized for the molecule, we can assume that it represents the best approximation in an independent-particle model. The filled-square curve corresponds to an equivalent calculation [12], but using a non-molecular-optimized atomic set. Therefore, in order to visualize the approximations introduced by our model we must compare our results with

TABLE III. Contribution (in hartrees) to the total energy of each term in the model Hamiltonian at the calculated equilibrium distance.

Contribution term	Type of calculation	LiH	BeH	BH	CH	NH	OH	FH
Diagonal	ORTH	−11.908	−21.334	−35.576	−55.079	−79.909	−111.12	−148.76
	S2	−11.974	−21.619	−35.905	−55.080	−79.611	−110.70	−148.21
Direct	ORTH	2.696	4.155	6.697	10.083	14.056	20.424	27.815
Coulombic	S2	2.717	4.173	6.585	9.786	13.749	19.966	27.372
Exchange	ORTH	0.619	1.418	2.778	5.171	8.762	12.459	17.533
Coulombic	S2	0.644	1.462	2.734	4.961	8.440	12.089	17.172
Hopping	ORTH	−0.363	−0.804	−0.856	−1.029	−1.032	−1.129	−1.198
	S2	−0.359	−0.838	−1.169	−1.292	−1.152	−1.263	−1.125
Spin-flip	ORTH	0.002	0.002	0.014	0.014	0.013	0.013	0.011
	S2	0.020	0.051	0.111	0.105	0.062	0.056	0.031
Nuclear	ORTH	1.000	1.481	1.852	2.609	3.182	4.000	4.737
repulsion	S2	1.000	1.600	2.381	3.158	3.500	4.444	4.737
Total	ORTH	−7.954	−15.081	−25.092	−38.232	−54.928	−75.354	−99.865
energy	S2	−7.952	−15.175	−25.262	−38.362	−55.011	−75.410	−100.02

those of this latter case, since both calculations use the same basis set. These are presented for both MH-ORTH and MH-S2 descriptions. From this comparison, we conclude that the many-body terms neglected in deriving Eq. (1) do not seem to be critical as far as the calculation of total energies is concerned. In comparison with the Cade-Huo results, we infer that the discrepancies are mainly due to the use of the different basis sets. The MH-S2 calculation tends to overestimate total energies with respect to the MH-ORTH and we can see that, in applying the MH-S2 model, the use of ghost atom orbitals becomes particularly relevant.

In Table II the binding energies of the different hydrides calculated at its equilibrium distances are shown for the following cases: (i) our MH-S2 calculation, (ii) our MH-ORTH calculation, and (iii) full all-electron HF calculation using atomic basis set [12]. The experimental binding energies are also included. Here we observe that the many-body Hamiltonian approximated by a superposition of bond-pair Hamiltonians in the HF approximation works fairly well in describing binding energies. The second-order expansion in S of the parameters leads to different effects in the binding energies, depending not only on the magnitude of the overlaps, but also on the kind of chemical bond, i.e., the amount of charge transfer involved. For nearly ioniclike systems (LiH,OH, and FH) the results from MH-S2 are in good agreement with those obtained using MH-ORTH, predicting binding energies smaller than the experimental values. For covalent systems MH-S2 leads to an underestimation of repulsive effects, consequently producing large binding energies, and gives the wrong trend when different hydrides of this type are compared. In this table the equilibrium distances, vibrational frequencies, and dipole moments for all the dimers according to each approximation are also shown.

The interaction energy curves for the BH, CH, and NH molecules are displayed in Fig. 3. In each case, the results from the model Hamiltonian [Eqs. (1) and (4)] are compared with those obtained by solving the complete Hamiltonian either by using an atomic basis set optimized [14] or nonoptimized [12] for molecules. In all cases it is verified that the expansion in S underestimates repulsive effects at all distances. This obviously leads to smaller equilibrium distances and to deeper wells.

Finally, Table III shows the contributions of the different terms of the model Hamiltonian to the total energy at the equilibrium distance for both options. Each row corresponds to a given term in either Eq. (1) or (4), respectively, i.e., the first row corresponds to the sum of E parameters, the second to the sums involving U and J, and the next one to the sum of $G = J - J^x$ terms. The contributions to the hopping T, spin-flip, and nuclear repulsion terms are displayed in the last three rows.

IV. CONCLUSIONS

A model based on a truncated second-quantized Hamiltonian, recently proposed to describe the interactions between adsorbates and solid surfaces as a bond-pair superposition between dimers, has been analyzed by applying this description to the hydrides of the first-row elements. We found the following. (i) The superposition of a bond-pair Hamiltonian in Eq. (1) gives results in fair agreement with those obtained from the complete Hamiltonian, as it follows from the comparison with the full all-electron molecular calculations [12]. (ii) The separated-atom limit situation is well described by the valence-bond nature of the model at large internuclear separations. (iii) The expansion of the Hamiltonian parameters, carried out consistently up to second order in the atomic overlaps, is a good approximation for nearly ionic hydrides: LiH, OH, and FH.

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