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Powerful effective one-electron Hamiltonian for describing many-atom interacting systems

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In this paper, we present an alternative way to build the effective one-electron picture of a many-atom interacting system. By simplifying the many-body general problem we present two different options for the bond-pair model Hamiltonian. We have found that the successive approximations in order to achieve the effective description have a dramatic influence on the result. Thus, only the model that introduces the correct renormalization in the diagonal term due to the overlap is able to reproduce, even in a quantitative fashion, the main properties of simple homonuclear diatomic molecules. The success of the model resides in the accurate definitions (free of parametrization) of the Hamiltonian terms, which, therefore, could be used to describe more complex interacting systems such as polyatomic molecules, adsorbed species, or atoms scattered by a surface.

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I. INTRODUCTION

The interaction between two atoms can be thought of as the fundamental knowledge in the study of many-atom interacting systems. Thus, a model able to describe intricate systems such as polyatomic molecules, adsorbed species, or atoms scattered by surfaces, in terms of a superposition of bond-pair interactions, becomes a very desirable objective. Most of the theoretical approaches concerning molecular modeling have put efforts to incorporating effects beyond the effective one-electron picture [1–3]. However, in this work we will show that lots of important ingredients reside at the effective one-electron picture level when the approximations are properly made.

Consequently, we are going to concentrate on the way of building a consistent model, which, starting from the elemental atom-atom interaction, provides a good basis for the description of more complex systems. The basic ideas of the model have already been presented and employed in quantum-chemistry calculations [4], in adsorption [5,6], (chemical and physical) and dynamical-charge-exchange processes [7,8]. Nevertheless, further analysis of the chemical features involved in the model (such as molecular-orbital symmetries, electronic configurations, etc.), have not been explored at present. No comparative analysis of the two possibilities that we have to build an effective Hamiltonian has been extensively discussed before. In this work we progress in this sense, and we find that the successive approximations, in order to achieve a good effective model, have a meaningful influence on the results.

In order to verify the capabilities of the proposal, we calculate the properties of very simple homonuclear dimers and compare our results with other standard and powerful theoretical formalisms such as the local-spin-density approximation (LSDA) and the full-electron unrestricted Hartree-Fock (HF) molecular-orbital (MO) calculations. In addition, we show that, contrarily to these methods, our proposal provides an overall description of the interaction process within a wide range of atom-atom separation distances, including the bonding and dissociation of atoms through the formation of molecular-orbital states.

This paper is organized as follows: in Sec. II we present the theoretical aspects of the alternative options of the many-body Hamiltonian for a two-atom interacting system, and the mean-field approximations performed in each case. In Sec. III the full-electron self-consistent calculation of the properties of diatomic molecules is described, while in Sec. IV the results for the homonuclear dimers of the first row are discussed and compared with the ones obtained from the LSDA and the usual MO calculations, and also with the experimental findings. Section V is devoted to the concluding remarks.

II. THEORY

A. A model for the atom-atom interaction

Our starting point is the second-quantized version of the many-body electronic Hamiltonian including electron-electron repulsion

$$\hat{H}=\sum_{i,j,\sigma} t_{ij}\hat{c}^{+}_{i\sigma}\hat{c}_{j\sigma}+\sum_{i,j,k,l,\sigma,\sigma'} v_{ijkl}\hat{c}^{+}_{i\sigma}\hat{c}_{j\sigma'}\hat{c}^{+}_{k\sigma}\hat{c}_{l\sigma'}, \qquad (1)$$

where the index i denotes the orthonormal atomic basis set $\{\phi_i\}$ and $\hat{n}_i=\hat{c}^{+}_i\hat{c}_i$ is the fermionic number operator. The parameters of the one- and two-electron terms of the Hamiltonian are

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

and

$$v_{ijkl}=\left\langle \phi_i(r)\phi_j(r')\left|\frac{1}{|r-r'|}\right|\phi_k(r)\phi_l(r')\right\rangle. \tag{3}$$

The following step is to neglect all terms involving four different spin-orbital states, except those related with spin-flip terms such as $\hat{c}^+_{j-\sigma}\hat{c}_{i-\sigma}\hat{c}^+_{i\sigma}\hat{c}_{j\sigma}$, and the result of this approximation is a many-body Hamiltonian written as a superposition of bond pairs

$$\hat{H}=\sum_{i,\sigma}\left[\varepsilon_i+\frac{1}{2}U_i\hat{n}_{i-\sigma}+\frac{1}{2}\sum_{j\neq i}(J_{ij}\hat{n}_{j-\sigma}+G_{ij}\hat{n}_{j\sigma})\right]\hat{n}_{i\sigma}+\sum_{i\neq j,\sigma}\left[\hat{T}^\sigma_{ij}+\frac{1}{2}J^x_{ij}\hat{c}^+_{j-\sigma}\hat{c}_{i-\sigma}\right]\hat{c}^+_{i\sigma}\hat{c}_{j\sigma}. \tag{4}$$

Here we have introduced the hopping operator $\hat{T}^\sigma_{ij}$,

$$\hat{T}^\sigma_{ij}=t_{ij}+\sum_k[h_{k,ij}\hat{n}_{k-\sigma}+(h_{k,ij}-h^x_{k,ij})\hat{n}_{k\sigma}], \tag{5}$$

and we have defined according with Eqs. (2) and (3): $\varepsilon_i=t_{ii}$, $U_i=v_{iiii}$, $J_{ij}=v_{ijij}$, $J^x_{ij}=v_{iijj}$, $G_{ij}=J_{ij}-J^x_{ij}$, $h_{k,ij}=v_{kikj}$, and $h^x_{k,ij}=v_{kijk}$.

Now we can perform a mean-field approximation of Eq. (4) by decoupling in the standard way the many-body operators. The one-electron effective Hamiltonian obtained in this form corresponds to option I.

The orthonormal basis set $\{\phi_i\}$ is constructed by following the symmetric orthogonalization procedure [9],

$$\phi_i=\sum_j(1+S)^{-1/2}_{ij}\varphi_j, \tag{6}$$

where φ_j is the atomic orbital (j labels both, the the type of orbital and the atom site) and the overlap matrix elements are defined by $S_{ij}=\langle\varphi_j|\varphi_j\rangle-\delta_{ij}$.

We will see now that the overlap provides an important guideline to construct an effective Hamiltonian that resembles the correct features consistently with the one-electron picture. On the other hand, the convenience of this basis set is based on two important concluding remarks emphasized in the Löwdin's work [9]: (i) *for an effective one-electron Hamiltonian operator* $\hat{H}_{\rm eff}$, *the problem of solving the secular equations including the overlap integrals* S_{ij} *can be reduced to the same form as it has in the simplified theory that neglects the overlap if the matrix* $\hat{H}_{\rm eff}$ *is replaced by the matrix* $\hat{H}_{\rm eff}=(1+S)^{-1/2}\hat{H}_{\rm eff}(1+S)^{-1/2}$. *(ii) The solution of the problem of constructing the molecular orbitals, when taking the overlap integrals into consideration, is the same as if we consider the orthonormalized functions given by Eq. (6).*

It is found that the diagonal term of an one-electron Hamiltonian has to respond to the following expression when a second-order overlap expansion is performed [10]:

$$\tilde{\varepsilon}_i=\varepsilon_i^0-\sum_j S_{ij}t_{ij}+\frac{1}{2}\sum_j S^2_{ij}(\varepsilon^0_i-\varepsilon^0_j), \tag{7}$$

where the super-index 0 denotes that the calculation of the respective parameter must be evaluated as in Eq. (2) but after replacing the orthonormal basis set by the atomic one. Here the one-electron hopping t_{ij} is maintained in the orthonormal basis set. If now, in the many-body Hamiltonian given by Eq. (4), we expand up to second order in the atomic overlap all the parameters, except the hopping operators $\hat{T}^\sigma_{ij}$, and retain consistently only those terms that lead to a superposition of bond-pair interactions, we arrive at option II of the many-body Hamiltonian. An expression completely equivalent to Eq. (4) is obtained,

$$\hat{H}^{II}=\sum_{i,\sigma}\left[\hat{\tilde{\varepsilon}}_{i\sigma}+\frac{1}{2}\tilde{U}_i\hat{n}_{i-\sigma}+\frac{1}{2}\sum_{j\neq i}(\tilde{J}_{ij}\hat{n}_{j-\sigma}+\tilde{G}_{ij}\hat{n}_{j\sigma})\right]\hat{n}_{i\sigma}+\sum_{i\neq j,\sigma}\left[\hat{T}^\sigma_{ij}+\frac{1}{2}\tilde{J}^x_{ij}\tilde{c}^+_{j-\sigma}\hat{c}_{i-\sigma}\right]\hat{c}^+_{i\sigma}\hat{c}_{j\sigma}, \tag{8}$$

where now the different terms are redefined in accordance with

$$\hat{\tilde{\varepsilon}}_{i\sigma}=\varepsilon^0_i-\sum_j S_{ij}\hat{T}^\sigma_{ij}+\frac{1}{4}\sum_j S^2_{ij}\Delta\hat{E}^\sigma_{ij}, \tag{9a}$$

$$\Delta\hat{E}^\sigma_{ij}=\left(\varepsilon^0_i+\sum_k J^0_{ik}\hat{n}_{k-\sigma}+\sum_{k\neq j}G^0_{ik}\hat{n}_{k\sigma}\right)-\left(\varepsilon^0_j+\sum_k J^0_{jk}\hat{n}_{k-\sigma}+\sum_{k\neq i}G^0_{jk}\hat{n}_{k\sigma}\right),$$

$$\tilde{U}_i=U^0_i-\sum_j S^2_{ij}J^{x0}_{ij}, \tag{9b}$$

$$\tilde{J}_{ij}=J^0_{ij}-S^0_{ij}J^{x0}_{ij}, \tag{9c}$$

$$\tilde{G}_{ij}=(J^0_{ij}-J^{x0}_{ij})(1+S^2_{ij}), \tag{9d}$$

$$\tilde{J}^x_{ij}=J^{x0}_{ij}-\sum_k(S_{ik}h^{x0}_{jik}+S_{jk}h^{x0}_{ijk})+\sum_k(S^2_{jk}J^{x0}_{ik}+S^2_{ik}J^{x0}_{jk})+\frac{3}{4}\sum_k(S^2_{ik}J^{x0}_{ij}+S^2_{jk}J^{x0}_{ij})+\frac{1}{2}S^2_{ij}(J^{x0}_{ij}+J^0_{ij}). \tag{9e}$$

One can see from Eqs. (9a) and (9b) that the diagonal term of the effective one-electron Hamiltonian has the same renormalization by overlap than the expression (7), but now involving also the two-electron interaction terms.

It is worth to note here that in this option II: (i) we have not changed the basis of the problem, $\hat{c}^+_{i\sigma}$ and $\hat{c}_{j\sigma}$ operate on the orthonormal basis set yet; (ii) the expressions given by Eqs. (9a)–(9e) are not simply the expansion up to second order in the overlap of each parameter, but these arise from a reordering of the different terms in order to achieve the induced overlap renormalizations expected within a correct effective one-electron picture.

Option II also offers the possibility of extending the model to large systems. The remaining question of how the hopping parameters defined within an orthonormal basis set are calculated in these cases was solved by constraining the orthogonalization to a dimeric subspace, this approximation being justified through a proposed treatment of the three-center integrals [11,5].

As in option I, the following step is to perform a mean-field approximation of Eq. (8) leading to an one-electron-like description. The typical expression of the effective electronic Hamiltonian in the second-quantized language is (in the Appendix we show the details of the mean-field approximation performed in both options)

$$\hat{H}_{\text{eff}}^{I,II}=\sum_{i\sigma}\zeta_{i\sigma}^{I,II}\hat{n}_{i\sigma}+\sum_{i\neq j,\sigma}(V_{ij,\sigma}\hat{c}_{i\sigma}^{+}\hat{c}_{j\sigma}+\text{H.c.}). \tag{10}$$

The final expressions for the diagonal parameter $\zeta_{i\sigma}^{I,II}$ are

$$\zeta_{i\sigma}^{I}=\varepsilon_{i\sigma}+U_i\langle n_{i-\sigma}\rangle^{I}+\sum_{j\neq i}(J_{ij}\langle n_{j-\sigma}\rangle^{I}+G_{ij}\langle n_{j\sigma}\rangle^{I})$$
$$+\sum_{k\neq j}[h_{ikj}\langle c_{k-\sigma}^{+}c_{j-\sigma}\rangle^{I}+(h_{ikj}-h_{ikj}^{x})\langle c_{k\sigma}^{+}c_{j\sigma}\rangle^{I}], \tag{11}$$

$$\zeta_{i\sigma}^{II}=\langle\hat{\tilde{\varepsilon}}_{i\sigma}\rangle+\tilde{U}_i\langle n_{i-\sigma}\rangle^{II}+\sum_{j\neq i}(\tilde{J}_{ij}\langle n_{j-\sigma}\rangle^{II}+\tilde{G}_{ij}\langle n_{j\sigma}\rangle^{II})$$
$$+\sum_{k\neq j}[h_{ikj}\langle c_{k-\sigma}^{+}c_{j-\sigma}\rangle^{II}+(h_{ikj}-h_{ikj}^{x})\langle c_{k\sigma}^{+}c_{j\sigma}\rangle^{II}]. \tag{12}$$

The symbol $\langle\hat{\tilde{\varepsilon}}_{i\sigma}\rangle$ indicates that the number operators $\hat{n}_{i\sigma}$ have been replaced by their corresponding average values $\langle\hat{n}_{i\sigma}\rangle$ in the Eq. (9a). The contributions $-S_{ij}\langle\hat{T}_{ij}^{\sigma}\rangle$ and $1/4S_{ij}^2\langle\Delta\hat{E}_{ij}^{\sigma}\rangle$ in the definition of $\langle\hat{\tilde{\varepsilon}}_{i\sigma}\rangle$ reflect the important effect of the overlap in the renormalization of the diagonal parameters. It is straightforward to see that only $\zeta_{i\sigma}^{II}$ resembles the overlap expansion of the one-electron problem, being this a direct consequence of the reordering done in the many-body version of option II [Eq. (8)]. This is not the case of $\hat{H}_{\text{eff}}^{I}$, where the mean-field approximation is performed before doing any expansion in the overlap. In consequence the correct renormalizations $-S_{ij}\langle\hat{T}_{ij}^{\sigma}\rangle$ and $1/4S_{ij}^2\langle\Delta\hat{E}_{ij}^{\sigma}\rangle$ of the diagonal terms are not recovered when the overlap expansion is afterwards performed. This fact makes an important difference between $\hat{H}_{\text{eff}}^{I}$ and $\hat{H}_{\text{eff}}^{II}$ in such a way that $\hat{H}_{\text{eff}}^{I}$ is not able to describe the binding of atoms in practically all the homonuclear dimers analyzed, while $\hat{H}_{\text{eff}}^{II}$ gives systematically a good description, as we are going to see in the forthcoming sections.

III. SELF-CONSISTENT FULL-ELECTRON HF CALCULATION

In the HF approximation, the ground state is described by a single determinant $|\Phi\rangle$ constructed by occupying with the N electrons the lowest-energy one-electron molecular-orbital states (MOs) $\{\Psi_{\alpha\sigma}\}$. These MOs are expanded in the orthonormal atomic basis $\{\phi_i\}$,

$$\Psi_{\alpha\sigma}=\sum_i a_i^{\alpha\sigma}\phi_i\,,$$

and consequently the density-matrix elements are given by

$$\rho_{ij}^{\sigma}=\sum_{\alpha\ occ}a_i^{\alpha\sigma *}a_j^{\alpha\sigma}=\langle\hat{c}_{i\sigma}^{+}\hat{c}_{j\sigma}\rangle,$$

where $\langle\hat{c}_{i\sigma}^{+}\hat{c}_{j\sigma}\rangle$ denotes the average value on the ground state $|\Phi\rangle$ of the fermionic operators creating and destroying electrons in the orthonormalized atomic states.

The self-consistent procedure starts at the separate atom limit for which the charge configuration is known: $\rho_{ij}^{\sigma}=\delta_{ij}$ for the occupied atomic states, and $\rho_{ij}^{\sigma}=0$ otherwise. The initial atomic-charge configurations follow from the application of Hund's rules to each atom for ensuring good dissociation products; and the spin component $\hat{S}_z$ of the molecule is selected by pairing the corresponding spin states of the atoms forming the dimer. For decreasing internuclear distances, the inputs ρ_{ij}^{σ} are taken as the corresponding self-consistent output values of the preceding point. In this form we are constructing the molecule up from the properties of the constituent atoms, and the self-consistency is achieved more efficiently. As $\rho_{ij}^{\uparrow}$ is different from $\rho_{ij}^{\downarrow}$ in general, the procedure employed is an unrestricted HF calculation.

The more appropriate minimal basis set of an atom is the set of the HF atomic orbitals. In the present work we use the HF atomic basis set calculated in terms of Gaussian-type orbitals (GTOs) by Huzinaga [12].

The total energy of the two-atom (AB) system is calculated for each internuclear distance $R=|R_A-R_B|$ as

$$E_{A-B}(R)=\sum_{\alpha\sigma\ occ}\epsilon_{\alpha\sigma}-[X]+\frac{Z_AZ_B}{R},$$

where $\epsilon_{\alpha\sigma}$ are the eigenvalues of the corresponding occupied MOs and $[X]$ symbolizes the whole set of terms to be substracted according with the mean-field approximation, and the last term is the nucleus-nucleus repulsion.

The interaction energy between atom A and atom B is defined as

$$E_{\text{int}}(R)=E_{A-B}(R)-(E_A+E_B),$$

being E_A and E_B the total energies of the isolated atoms A and B, respectively.

The magnitudes chosen to characterize each dimer are the binding energy (E_b), the equilibrium distance (R_e) and the vibrational frequency (ω_e). The E_b and R_e values are obtained directly from the interaction energy curve $E_{\text{int}}(R)$,

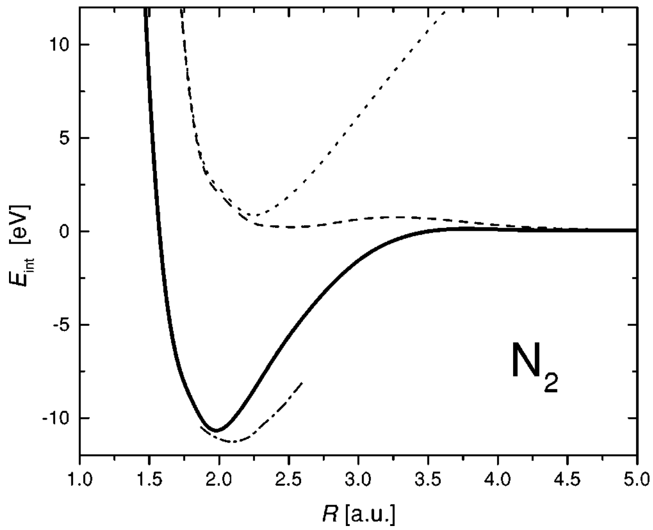

FIG. 1. Interaction energy for the N_2 system. (——) option II of the effective Hamiltonian, (— — —) option I of the effective Hamiltonian, (· · · ·) unrestricted HF MO calculation, (—·—·—·—) LSDA calculation from Ref. [13].

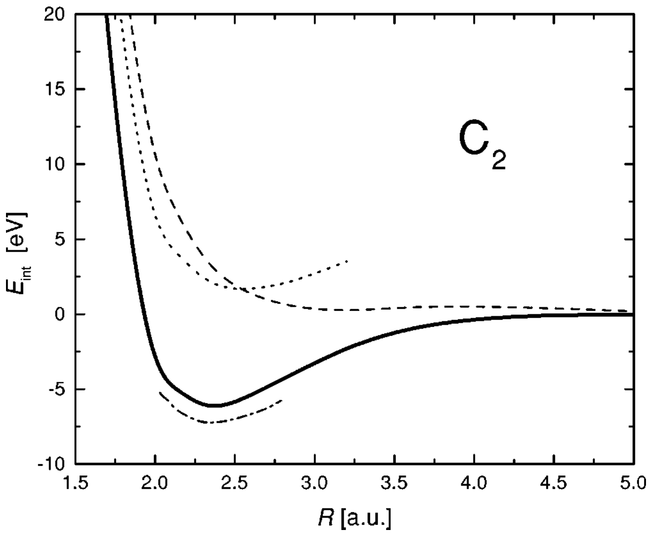

FIG. 2. Interaction energy for the C_2 system. The same as in Fig. 1.

while ω_e is evaluated from the harmonic approximation of the Morse potential that fits the calculated results.

IV. RESULTS AND DISCUSSION

The energy interaction curves $E_{\text{int}}(R)$ for Li_2, Be_2, B_2, C_2, N_2, and O_2 were calculated and compared with the ones obtained by Painter and Averill [13] within the local-spin-density approximation by using the exchange-correlation functional parametrized by Vosko, Wilk, and Nusair [14] (LSDA-VWN); and also with a quantum-chemistry MO calculation (QCMO) [15]. This last option, QCMO, was calculated with the GAUSSIAN98 code selecting an unrestricted HF approximation and using the same GTOs basis set that in our model calculation. Here, we present and discuss in detail the results obtained for N_2 (Fig. 1) and C_2 (Fig. 2), the discussion for the other systems is similar. The first point to notice from Figs. 1 and 2, is the good dissociation limit shown by our calculated curves, this being an expected result because the noninteracting atoms are the input for our calculation of $E_{\text{int}}(R)$. With the only exception of Li_2, option I and the QCMO calculations are unable to describe the binding and show a loss of continuity in the self-consistent procedure in some cases. On the other hand, option II of the effective Hamiltonian provides satisfactory results for all the analyzed dimers. Besides, our results compare quite good with the LSDA energy curves, in the range of distances where this comparison is possible.

It is also important to remark that the nonpolar character of the bonding is only ensured by option II in all the homonuclear dimeric systems.

In Table I, we summarize the equilibrium properties E_b, R_e, and ω_e that were extracted from the interaction curves. We include also the results of the $X\alpha$ model [16], and the experimental values [17]. We can observe that the values obtained from option II for each property are in very good agreement with the experimental values and with the theoretical results from the LSDA and $X\alpha$. The major disagreement is in the Be_2 system, in which there is not experimental evidence of its stability but all the theoretical models, including ours, predict a stable molecule.

A. About the ground state of the molecule by using an effective Hamiltonian

We will discuss here the results concerning the molecular-orbital properties of the ground state. First, we remark the differences between the one-electron picture and an effective one. In the one-electron description and considering unhybridization between $2s$ and $2p$ states, it is expected that: (i) in the separated atom limit, the energies of the up states are equal to the down states for each atom (ii) the two atoms are indistinguishables, i.e., the exchange of A and B does not modify the relative weight of each atomic state in the molecular orbital; (iii) in the C_2 and N_2 systems, the electronic configuration follows an ordering in energy such as $(1\sigma_g)(1\sigma_u)(2\sigma_g)(2\sigma_u)(1\pi_u)(3\sigma_g)$ [18].

Due to the electronic Coulomb repulsion within a mean-field approximation, the effective scheme is clearly different from the one-electron one. For simplicity we analyze from the expressions of $\zeta_{i\sigma}^{I,II}$ [Eqs. (11) and (12)] only how the $J_{ij}\langle n_{j-\sigma}\rangle$ term acts. This kind of term represents the coulomb repulsion between the electronic charge density centered on the i state and another charge density centered on the j state. This positive contribution will renormalize the atomic-energy level with spin σ, when the j state is occupied with an electron with spin $-\sigma$. In an open-shell atom such as nitrogen, the maximum multiplicity requirement leads to ubicate the three p electrons with the same spin projection, we say up. Hence, the down p states feel the repulsion given by $J_{ij}\langle n_{j\uparrow}\rangle$, but not the up p states since $\langle n_{j\downarrow}\rangle$ are equal to zero. This reasoning is also valid for the s states. In Figs. 3 and 4 we show the electronic configurations of the separate atom and bounded situations for each spin projection in the cases

TABLE I. Binding energy (E_b) is expressed in eV, equilibrium distance (R_e) in a.u., and frequency (ω_e) in cm^{-1}.

		Option I	Option II	LSDA	$X\alpha$	QCMO	Expt.
Li_2	R_e	5	4.5	5.12	5.12	5.4	5.05
	E_b	0.36	0.42	1.01	0.21		1.03
	ω_e		350	347	336		351
Be_2	R_e		4	4.63	4.58		
	E_b		0.86	0.5	0.43		
	ω_e		684	362	484		
B_2	R_e	3.81	3	3.03	3.03	5.2	3.04
	E_b	0.39	5.32	3.93	3.79		2.9
	ω_e		1095	1082	1078		1051
C_2	R_e		2.3	2.36	2.36	2.5	2.35
	E_b		6	7.19	6		6.2
	ω_e		1781	1869	1955		1857
N_2	R_e	2.6	2	2.08	2.08	2.25	2.07
	E_b		10.66	11.34	9.09		9.91
	ω_e		2927	2387	2429		2358
O_2	R_e		2.1	2.31	2.28	2.5	2.28
	E_b		5	7.54	7.01		5.2
	ω_e		1756	1536	1610		1580

of N_2 and C_2 molecules, respectively. We can observe that the effective picture yields necessarily an asymmetric situation even for homonuclear molecules and, therefore, the hybridization between *s*- and *p*-states is unavoidable. Therefore, the relative ordering of σ and π molecular states can change, varying also in this form their bonding or antibonding character.

In both options the electronic configurations of the isolated atoms are the input in our calculation. The good dissociation limit is obtained by obeying the Hund's rule in each atom. The eigenstates of $\hat{H}^{I,II}_{\mathrm{eff}}$ are also eigenstates of the $\hat{S}_z$ component of the total spin operator, but they are not of $\hat{S}^2$. Then, for the case of partially filled shells in the atoms we can choose either a maximum or a minimum multiplicity state for the molecule.

1. Dimer N_2

The $^1\Sigma_g$ spectral term for the ground state of N_2 is obtained in this form by starting the self-consistent calculation with the following electronic configuration (the molecule is oriented along the *z* axis): $N(1s^2 2s^2 2p_{x\uparrow} 2p_{y\uparrow} 2p_{z\uparrow}) + N(1s^2 2s^2 2p_{x\downarrow} 2p_{y\downarrow} 2p_{z\downarrow})$. This is the only possible determinantal configuration for describing the good dissociation limit. Thus, our calculation implies basically an unrestricted self-consistent MO calculation in the cases of open-shell atoms.

However, in Fig. 3 we see that for the equilibrium distance ($R \simeq 2$ a.u.), the MOs as linear combinations of the orthonormalized atomic orbitals result to be equal for the two-spin components. The starting unrestricted MO calculation becomes a restricted one near the equilibrium distance when it has been imposed $S_z = 0$ for the state of the molecule. From the comparison between Figs. 3(a) and 3(b) we can observe that although the separate atom limit is the same for both options, the resulting MOs are quite different. Option II gives systematically MO energies lower than those given by option I for all the molecular states. In addition, the ordering of $(3\sigma_g)$ and $(1\pi_u)$ is exchanged.

In the one-electron picture, it is usual to define a qualitative quantity, the bond order, as the difference between bonding and antibonding electrons divided by two [19]; the value of the bond order being larger for more strongly bounded molecules. Taking this qualitative idea, we see that in option II there are eight bonding electrons and two antibonding and consequently the number of bonds is three. On the other hand, in option I, the bonding or antibonding character of each MO is less clear, but it seems that the $(3\sigma_g)$ MO has an antibonding character which favors a reduction of the bond order (and its binding energy).

2. Dimer C_2

In the C_2 molecule the situation is more complex, from both, the theoretical and the experimental points of view. The spectroscopy data indicates the existence of a strong band in the visible (the Swan band) related with the transition from a $^3\Pi_u$ state to a $^3\Pi_g$ state for C_2 vapor [20]. Then, the molecular symmetry indicates that the corresponding electronic configuration should be $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^3(3\sigma_g)^1$. This configuration comes evidently from the electron-electron interaction, such ordering not being possible in the one-electron picture. A $^3\Pi_u$ state can be achieved from the following electronic configuration in the separate-atom limit: $C(1s^2 2s^2 2p_{x\uparrow} 2p_{y\uparrow}) + C(1s^2 2s^2 2p_{x\downarrow} 2p_{z\downarrow})$. The curves in Fig. 2 and the values in Table I correspond to this configuration. In Figs. 4(a) and 4(b) we show the energy-level

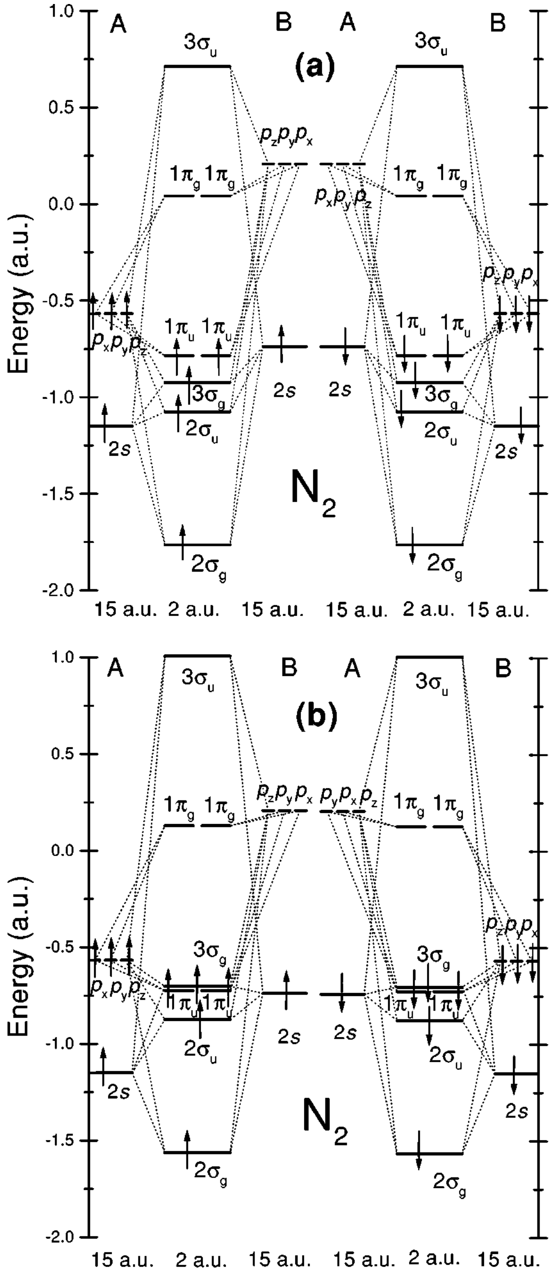

FIG. 3. MO energy scheme for the separate atom and bounded situations for the N_2 system. (a) Option II of the effective Hamiltonian; (b) option I of the effective Hamiltonian. Left panel corresponds to up electrons and right panel to down electrons.

scheme for both options of calculation. Here, the power of the effective-field description is clearly evidenced. Each electron feels a different mean field, and in consequence, it is possible to find a situation in which the $3\sigma_g$-down electron has lower energy than the $1\pi_u$ one, but the contrary is true for up electrons. Regarding the comparison between the two options of calculation, we conclude the same that in the N_2 molecule, option I gives systematically higher molecular energies and the MO $(3\sigma_g)$ has an antibonding character, which may be indicative of a nonbounded situation due to the reduction of the bond order.

In the one-electron description, the crossover point between $(1\pi_u)$ and $(3\sigma_g)$ orbitals is close to the stability position of the molecule. Then, a $^1\Sigma_g$ state for the C_2 molecule arising from a configuration such as $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$ is another possibility to be analyzed. In fact, this state is observed in the C_2 spectrum, but because of the selection rules, the relative position to the $^3\Pi_u$ state is unknown [21]. A $^1\Sigma_g$ state can be prepared in two ways. One of this is (obviously p_x can be exchanged by p_y): $C(1s^2 2s^2 2p_{x\uparrow} 2p_{z\uparrow}) + C(1s^2 2s^2 2p_{x\downarrow} 2p_{z\downarrow})$. The binding energy obtained with this configuration is $E_b = 9$ eV, and the electronic configuration is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2$. The MO energy

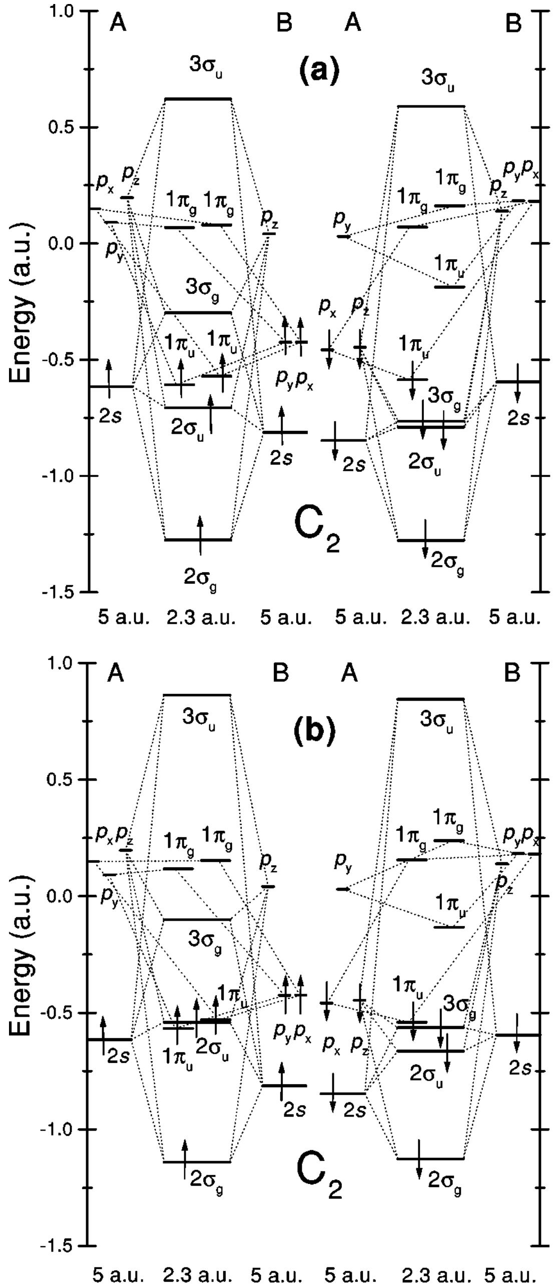

FIG. 4. MO energy scheme for the separate atom and bounded situations for the $^3\Pi_u$ spectral term of C_2. (a) Option II of the effective Hamiltonian; (b) option I of the effective Hamiltonian. Left panel corresponds to up electrons and right panel to down electrons.

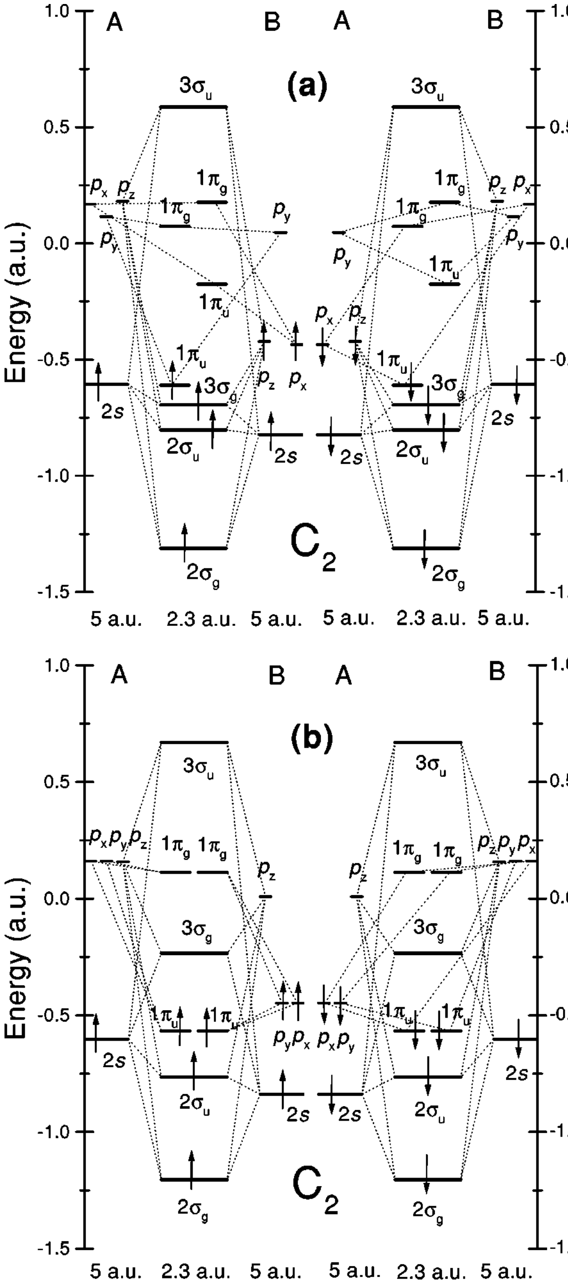

FIG. 5. MO energy scheme for the separate atom and bounded situations for the $^1\Sigma_g$ spectral term of C_2. (a) $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2$ electronic configuration; (b) $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$ electronic configuration. Both results from option II. Left panel corresponds to up electrons and right panel to down electrons.

scheme is included in Fig. 5(a). The other electronic configuration that also fulfills the symmetry requirement is C$(1s^22s^22p_{x\uparrow}2p_{y\uparrow})$+C$(1s^22s^22p_{x\downarrow}2p_{y\downarrow})$. In this case we obtain a binding energy around 3 eV and the electronic configuration is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4$. The corresponding energy-level scheme is included in Fig. 5(b). Therefore, from these results one concludes that a combination of equally weighted initial configurations that provide the correct dissociation products has to be the more appropriate proposal. In this way a binding energy between 3 eV and 9 eV would be expected for the C_2 molecule, but this means to do interaction of configurations that is out of the scope of this work.

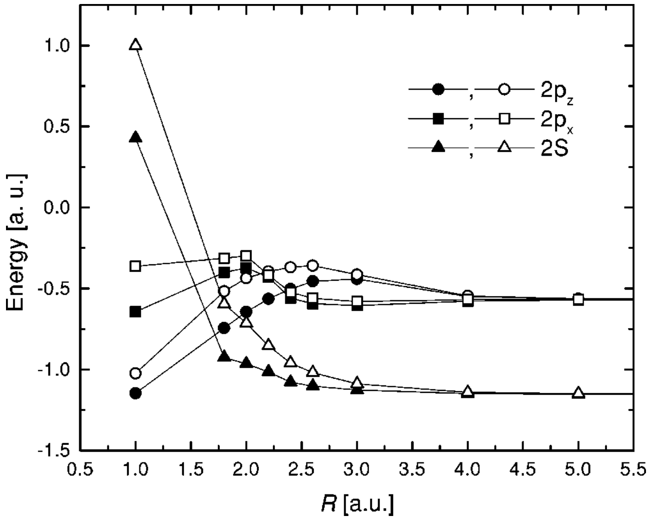

FIG. 6. Diagonal terms of the Hamiltonian for $2s$, $2p_x$, and $2p_z$ states of the N atom in the homonuclear dimeric system. Option II (full symbols); option I (empty symbols).

B. Energy parameters and transferability to more complex systems

The main difference between the two options resides in the approximation of the diagonal term of the Hamiltonian $\zeta_{i\sigma}$. The hopping term is essentially the same, the differences come only from the self-consistent calculation. In Fig. 6 we show the evolution of $\zeta^I_{i\sigma}$ and $\zeta^{II}_{i\sigma}$ for $i=2s$, $2p_x$, and $2p_z$ states of the N atom in the homonuclear dimeric system. Consistently with the previous results, it is observed that the repulsive contribution in option I is stronger than in option II. This fact is then reflected in a nonbounded situation for the molecule described by option I. From the point of view of the transference of these Hamiltonian parameters to more complex systems, as for instance, dynamical resonant processes of charge transfer between a moving atom and a surface (atom-surface scattering processes), the energy terms calculated by either one or another model Hamiltonian can lead to very different results for the final charge states of the atom [22]. The resonant mechanism of charge transfer depends strongly on the variation of the energy atom level with respect to the band-energy levels of the surface. Then, an accurate description of the energy Hamiltonian parameter is necessary for ensuring a good description of the dynamical process. And the way we have to decide for the best calculation of the Hamiltonian parameters is through an exhaustive study of the atom-atom interaction in dimeric systems. In this sense we argue that a good mean-field description as option II for the many-body Hamiltonian, which retains the basic physics, is an appropriate model to describe the interaction in many-atom systems.

V. CONCLUSIONS

A many-body Hamiltonian written in a second quantized language and using a symmetrically orthonormalized basis set allows to introduce the correct renormalizations by the overlap in the diagonal terms of the effective one-electron Hamiltonian. This effective Hamiltonian responds to a superposition of bond-pair interactions, with diagonal and nondiagonal terms well defined up from the one-and two-electron integrals defined within the atomic basis set. It was shown through the study of diatomic molecules, that the correct renormalizations of the diagonal terms by the overlap expected within a one-electron picture, and the consistency with a bond-pair interaction model maintained when the overlap expansion is performed, ensure a very good balance between the repulsive and attractive contributions in the self-consistent calculation of the total energy of the system.

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APPENDIX: MEAN-FIELD APPROXIMATION

The one-electron effective Hamiltonians within the two options I and II are constructed by performing a mean-field approximation over the many-body Hamiltonians given by Eqs. (4) and (8), respectively. The typical expression of the effective Hamiltonian,

$$\hat{H}_{\mathrm{eff}}=\sum_{i\sigma}\zeta_{i\sigma}\hat{n}_{i\sigma}+\sum_{i\neq j,\sigma}(V_{ij,\sigma}\hat{c}^{+}_{i\sigma}\hat{c}_{j\sigma}+\mathrm{H.c.})+V_{n-n},$$

is obtained by the following procedure in each case.

1. Option I

A complete mean-field approximation is performed over the all two-electron terms of Eq. (4) arriving to the corresponding HF version with the Hamiltonian parameters defined as

$$\zeta^{I}_{i\sigma}=\varepsilon_i+U_i\langle n_{i-\sigma}\rangle+\sum_{j\neq i}(J_{ij}\langle n_{j-\sigma}\rangle+G_{ij}\langle n_{j\sigma}\rangle)$$

$$+\sum_{k\neq j}[h_{ikj}\langle c^{+}_{k-\sigma}c_{j-\sigma}\rangle+(h_{ikj}-h^{x}_{ikj})\langle c^{+}_{k\sigma}c_{j\sigma}\rangle],$$

$$V^{I}_{ij,\sigma}=\langle\hat{T}^{\sigma}_{ij}\rangle-G_{ij}\langle c^{+}_{j\sigma}c_{i\sigma}\rangle+J^{x}_{ij}\langle c^{+}_{i-\sigma}c_{j-\sigma}\rangle$$

$$-\sum_{k}[(h_{ikj}-h^{x}_{ikj})\langle c^{+}_{k\sigma}c_{i\sigma}\rangle+(h_{jik}-h^{x}_{jik})\langle c^{+}_{j\sigma}c_{k\sigma}\rangle],$$

where

$$\langle\hat{T}^{\sigma}_{ij}\rangle=t_{ij}+\sum_{k}[h_{kij}\langle n_{k-\sigma}\rangle+(h_{kij}-h^{x}_{kij})\langle n_{k\sigma}\rangle].$$

2. Option II

Here, a mean-field calculation is also performed over the two-electron terms of Eq. (8), except the $\hat{\tilde{\varepsilon}}_{i\sigma}\hat{n}_{i\sigma}$ terms that are considered within the average form $\langle\hat{\tilde{\varepsilon}}_{i\sigma}\rangle\hat{n}_{i\sigma}$. The expressions found for the diagonal and off-diagonal terms of $\hat{H}_{\mathrm{eff}}$ are in this case

$$\zeta^{II}_{i\sigma}=\langle\hat{\tilde{\varepsilon}}_{i\sigma}\rangle+\tilde{U}_i\langle n_{i-\sigma}\rangle+\sum_{j\neq i}(\tilde{J}_{ij}\langle n_{j-\sigma}\rangle+\tilde{G}_{ij}\langle n_{j\sigma}\rangle)$$

$$+\sum_{k\neq j}[h_{ikj}\langle c^{+}_{k-\sigma}c_{j-\sigma}\rangle+(h_{ikj}-h^{x}_{ikj})\langle c^{+}_{k\sigma}c_{j\sigma}\rangle],$$

$$V^{II}_{ij,\sigma}=\langle\hat{T}^{\sigma}_{ij}\rangle-\tilde{G}_{ij}\langle c^{+}_{j\sigma}c_{i\sigma}\rangle+\tilde{J}^{x}_{ij}\langle c^{+}_{i-\sigma}c_{j-\sigma}\rangle$$

$$-\sum_{k}[(h_{ikj}-h^{x}_{ikj})\langle c^{+}_{k\sigma}c_{i\sigma}\rangle+(h_{jik}-h^{x}_{jik})\langle c^{+}_{j\sigma}c_{k\sigma}\rangle],$$

where $\langle\hat{\tilde{\varepsilon}}_{i\sigma}\rangle$ is defined as

$$\langle\hat{\tilde{\varepsilon}}_{i\sigma}\rangle=\varepsilon^{0}_{i}-\sum_{j}S_{ij}\langle\hat{T}^{\sigma}_{ij}\rangle+\frac{1}{4}\sum_{j}S^{2}_{ij}\langle\Delta\hat{E}^{\sigma}_{ij}\rangle,$$

with

$$\langle\Delta\hat{E}^{\sigma}_{ij}\rangle=\left(\varepsilon^{0}_{i}+\sum_{k}J^{0}_{ik}\langle\hat{n}_{k-\sigma}\rangle+\sum_{k\neq j}G^{0}_{ik}\langle\hat{n}_{k\sigma}\rangle\right)$$

$$-\left(\varepsilon^{0}_{j}+\sum_{k}J^{0}_{jk}\langle\hat{n}_{k-\sigma}\rangle+\sum_{k\neq i}G^{0}_{jk}\langle\hat{n}_{k\sigma}\rangle\right),$$

and the $\langle\hat{T}^{\sigma}_{ij}\rangle$ have the same formal expression as in option I.

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