PHYSICAL REVIEW A VOLUME 32, NUMBER 1 JULY 1985

Derivation of model Hamiltonians: Exchange Hamiltonian for H_2

Carlos E. Solivérez*
Centro Atómico Bariloche, Comisión Nacional de Energía Atómica, 8400 Bariloche, Río Negro, Argentina
and Instituto Balseiro, Comisión Nacional de Energía Atómica y Universidad Nacional de Cuyo,
8400 Bariloche, Río Negro, Argentina

Eduardo R. Gagliano
Instituto de Desarrollo Tecnológico para la Industria Química,
Consejo Nacional de Investigaciones Científicas y Técnicas, Casilla de Correo 91,
3000 Santa Fe, Santa Fe, Argentina

Gustavo A. Arteca
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, División Química Teórica,
Consejo Nacional de Investigaciones Científicas y Técnicas, Sucursal 4, Casilla de Correo 16,
1900 La Plata, Buenos Aires, Argentina

(Received 10 August 1984)

The derivation of model Hamiltonians such as crystal-field and spin Hamiltonians requires the decoupling of electrons, which may be done by defining an appropriate equivalent Hamiltonian H_{eq}. The connection between H_{eq} and the original Hamiltonian, and between the respective eigenfunctions, is explicitly given. The eigenfunctions of H_{eq} are linear combinations of simple products of atomic spin orbitals, the latter being chosen in such a way that its antisymmetrization leads to a linearly independent set. The problem is then reformulated in a chosen subspace (effective space) via the effective-Hamiltonian formalism. The model Hamiltonian H_{mod} is then obtained by projecting out the undesired degrees of freedom. If in the two-atom two-electron case one keeps in H_{mod} only first-order terms in the interatomic interaction, one gets the usual Heitler-London approximation. For this reason the formulation has been called the extended Heitler-London method. As an illustration the formalism is applied to the H_2 molecule, where the usual Heisenberg Hamiltonian is rigorously derived and the values of the energy baricenter and magnetic exchange constant are given, up to the second order of perturbation theory.

I. INTRODUCTION

The first step towards a microscopic description of a solid-state system is the formulation of an appropriate model Hamiltonian H_{mod}. This Hamiltonian has to be contrasted with—or have its parameters adjusted from—the results of a certain set of experiments. As these experiments cover a well-defined energy range, one needs only to look at a known number n of energy eigenvalues of H_{mod} with known degeneracies. One may therefore define H_{mod} in such a way that it operates within an n-dimensional vectorial space Ω_{mod}. The problem is that the basis functions which span Ω_{mod} are not known *a priori*.

When doing, for instance, near-ultraviolet electronic spectroscopy of Cu^{2+} ions in solids it is known that the levels of interest stem from the ground multiplet ^2D, so that one needs only to consider a 2×5-dimensional space. But this space is not the one spanned by the ionic d orbitals and the $s=\frac{1}{2}$ spinors, because electric dipole transitions would then be forbidden by Laporte's rule, which is known not to be the case. It is therefore necessary to invoke admixtures with at least one excited configuration.[1] One may nevertheless, as is customarily done by experimentalists, define a model Hamiltonian within the model space Ω_{mod} spanned by the ^2D eigenfunctions of the free Cu^{2+} ion.

The given example clearly shows that—apart from its dimension—the model space Ω_{mod} may be chosen quite freely. As the eigenvalues of H_{mod} should be equal to a set of eigenvalues of the actual Hamiltonian H—a set which depends on the experiments performed on the system—it is clear that H_{mod} does not coincide with H. The theoretician is therefore confronted with the task of establishing an explicit connection between the model and the actual eigenvalue problem.

If the task involved only the reduction of the dimension of the domain of H while preserving at the same time all the degrees of freedom of the system, the solution would be easily obtained. In this particular case H_{mod} would be a suitably defined effective Hamiltonian associated both with H and a reference Hamiltonian determined by the available experimental data (see Appendix B for a more thorough discussion of effective Hamiltonians).

That this is not the general case is clearly shown by the Cu^{2+} example where, due to the nonvanishing overlap, one cannot neglect the effect of the ligand's electrons. It is in fact the interaction with these electrons which gives the main contribution to the crystal-field parameters.[2] One has therefore not only to work in a reduced domain, but also to get rid of a given number of degrees of freedom.

The problem of deriving model Hamiltonians in the case where the kept and the discarded dynamical variables correspond to nonidentical particles has been fully discussed in a previous paper.[3] It was shown there—a result which is also valid for identical particles—that a necessary condition for the existence of a meaningful model Hamiltonian is that the state of the subsystem of disposable particles be nondegenerate. By "meaningful" it is here meant that H_{mod} should give not only the actual energy eigenvalues but also determine in the usual way the time evolution of all physical magnitudes. The classical interpretation of the nondegeneracy condition is that the omitted particles then play the role of a scleronomous constraint which determines the values of the parameters of the subsystem under study. For a more detailed discussion of this point the reader is referred to the Appendix and the end of Sec. V of the aforementioned paper.[3]

Under the previously given condition H_{mod} can be expressed as the mean value of a suitably defined effective Hamiltonian, there being an explicit connection between the model eigenfunction and the actual one. Unfortunately the prescription does not apply to the case where the retained and the omitted dynamical variables belong to indistinguishable particles. The reason for this failure is that one may get rid of the latter only when they can be fully factorized in the wave function, which does not happen for symmetric or antisymmetric wave functions where the variables are inextricably admixed.

Due to this difficulty the few theoreticians concerned with the justification of model Hamiltonians such as crystal-field Hamiltonians and the spin Hamiltonians which describe the magnetic properties of solids,[4] have looked only at their eigenvalues, disregarding the problem of the relationship between the actual and model eigenfunctions. Stevens wrote, for instance, "the operators in a spin Hamiltonian are equivalent operators which reproduce the energy levels, but not the eigenstates. There may be a connection between the states, but what it is is often obscure."[5] In his discussion of direct exchange effects, Herring[6] points out that the correspondence between the actual and model Hamiltonians is not a projection—as is the case for nonidentical particles—but a more general mapping defined by the equality of certain matrix elements [see the first paragraph of p. 22 and Eq. (3.5) of his paper]. Although Herring realizes that a suitable choice for model wave functions is the Heitler-London one,[7] he does not pursue the idea to the very end, probably due to the difficulty of introducing the necessary higher-order corrections.[8] He chooses to introduce an *ad hoc* potential with the desired physical features instead of explicitly deriving it from the mapping.

To our knowledge the first significant advance in the last direction was made by Eremin and co-workers in connection with the derivation of crystal-field Hamiltonians.[9] Several important steps were overlooked in their derivation which is also obscured by its perturbative nature and the apparently inconsistent use of orthonormalization schemes. The formulation we present here overcomes these limitations, at least for the two-electron case, this being the first step towards a discussion of many-electron and many-atom systems. Although we will illustrate the formalism with the simplest known spin Hamiltonian, the Heisenberg Hamiltonian describing the exchange splitting of the H_2 molecule's ground state, the same scheme may be used for the derivation of any model Hamiltonian.

All present calculations of electronic structure require choosing some specific basis set, the first successful attempt being that of Heitler and London[7] in the early days of quantum mechanics. Their choice of atomic spin orbitals was surely dictated by the chemists' traditional view of molecules as being built up from atoms. The soundness of this atoms-in-molecules approach becomes evident as soon as one realizes that the interatomic interactions are a small fraction of the total molecular energy.[10,11] One therefore guesses that the original Heitler-London approximation is the first-order contribution in a perturbative calculation, a guess that we show here to be correct. A similar argument applies to atoms in solids as long as its number N is kept small, and even when N goes to infinity if due care is taken when performing the expansions.[12]

The extended Heitler-London method which we are about to develop has several advantages. First, it may be used to rigorously justify model Hamiltonians like the crystal-field and the spin (exchange) Hamiltonians previously discussed. Second, it contains the important correlation effects[11] that are necessarily absent in any molecular-orbital formulation because of its intrinsic independent-electron nature. Third, it provides a systematic way of analyzing solid-state trends in terms of the known properties of the constituent atoms, a feature which would be lacking in any fully *ab initio* calculation.

The method is based upon three main ideas which are convenient to briefly discuss in advance in order to put in proper perspective the somewhat abstract mathematical formulation that follows.

(1) The mathematical complications introduced by the antisymmetry constraints are eliminated by introducing a new Hamiltonian which forces the wave functions to be antisymmetric. This requires to reduce the domain of the actual Hamiltonian H so that there is a one-to-one correspondence between the original antisymmetrical basis functions and the new ones. The resulting new Hamiltonian explicitly shows the spin dependence of the energy which is the consequence of the exchange interaction. When one naturally chooses as the new basis a set of simple products of spin orbitals, the way is paved for a decoupling of the electrons. In the case of an orbitally nondegenerate ground state, the scheme automatically leads to an exchange Hamiltonian[4] which in the two-electron case exactly reduces to the usual Heisenberg Hamiltonian.

(2) The lack of orthogonality of the aforementioned basis introduces the complication that the matrix representations used in actual calculations do not preserve the standard form of the eigenvalue equation. This standard form is restored by using symmetric orthonormalization operators, which at the same time preserve both the system's symmetry properties and the unitary character of some operators.

(3) In order to link our formulation with the model Hamiltonians used in practice, it is necessary to restrict the problem to a proper effective subspace. This is made

by using the effective-Hamiltonian formalism, in either an exact or a perturbative fashion.[13,14] This is the same as first working with some selected set of functions, and then introducing the corrections induced by the neglected ones.

In order to work with the desired model basis one has to eliminate some degrees of freedom keeping at the same time an explicit connection between the primitive and final basis functions. One then finds the eigenvalues and eigenfunctions of the resulting new Hamiltonian H_{mod} by using symmetry arguments and solving the usual secular equation. The eigenvalues thus found coincide with those of H, and the actual wave functions are in a one-to-one correspondence with the eigenfunctions of H_{mod}. This is in agreement with the usual practice of writing model Hamiltonians whose domain is some freely selected model subspace chosen from experimental arguments.

The paper's organization is as follows. Starting with the general formulation, we then apply it to the H_2 molecule in the approximation corresponding to the standard Heitler-London approach. After showing how one rigorously obtains in this case a Heisenberg Hamiltonian, we next discuss the introduction of the excited states, explicitly giving the second-order perturbative approximation.

II. FORMALISM

Consider the following simple products of atomic spin-orbitals:

$$\Psi(1,2,\ldots,N)=\psi_1(1)\psi_2(2)\cdots\psi_N(N)\ , \tag{2.1}$$

$$\psi(j)=\varphi(\mathbf{r}_j)\chi(\sigma_j)\ , \tag{2.2}$$

where $\mathbf{r}$ and σ are the electronic coordinates and spin. The corresponding antisymmetrized products are $A\Psi$, where the antisymmetrizer A is given by[15]

$$A=\sum_P pP/N!\ . \tag{2.3}$$

The sum runs over the $N!$ permutations P of N electrons, p being 1 for the even permutations, and -1 for the odd ones. The antisymmetrizer A is a projection operator which has the following properties:

$$A^{\dagger}=A\ , \tag{2.4}$$

$$A^2=A\ , \tag{2.5}$$

$$AP=PA=pA\ . \tag{2.6}$$

If the set of simple products $\{\Psi\}$ is properly chosen—a problem which we discuss below—the corresponding set $\{A\Psi\}$ is a basis for the expansion of the molecular wave function obtained from the eigenvalue equation

$$Hu=Eu\ , \tag{2.7}$$

where

$$Au=u\ , \tag{2.8}$$

$$u=\sum_p c_p A\Psi_p\ . \tag{2.9}$$

As we will disregard relativistic effects, H is spin independent, thus commuting with the dimensionless total electronic spin angular momentum operator $\mathbf{S}$. Therefore u may be taken to be an eigenfunction both of $\mathbf{S}^2$ and S_z. It is thus convenient to take instead of the simple products Eq. (2.1) the linear combinations

$$\Psi_p(1,2,\ldots,N)$$
$$=\Phi_{j(S)}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\chi_{SM}(\sigma_1,\sigma_2,\ldots,\sigma_N)\ , \tag{2.10}$$

where

$$\Phi_j(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\varphi_1(\mathbf{r}_1)\varphi_2(\mathbf{r}_2)\cdots\varphi_N(\mathbf{r}_N)\ , \tag{2.11}$$

$$\langle\chi_{SM}\,|\,\chi_{S'M'}\rangle=\delta_{SS'}\delta_{MM'}\ , \tag{2.12}$$

$$\mathbf{S}^2\chi_{SM}=S(S+1)\chi_{SM},\quad S_z\chi_{SM}=M\varphi_{SM}\ . \tag{2.13}$$

The orbital part $\Phi_{j(S)}$ in general will depend on the total spin S as illustrated by Eq. (C9). In what follows each function of the kind Eq. (2.10) will be called an orbitally simple product (OSP), p and j standing for a whole set of indices. The corresponding antisymmetrized product (AP) is

$$f_p=A\Psi_p\ . \tag{2.14}$$

The basis $\{\Psi_p\}$ of OSP's should be defined in such a way that all AP's derived from Eq. (2.14) are linearly independent. This means that no OSP should be included that under an exchange of arguments is either invariant or identical to any other OSP in the set. In the first case the corresponding AP vanishes (exclusion principle), while in the second the corresponding AP's differ from each other at most in sign, as follows from the property Eq. (2.6). A simple prescription for generating such a basis is to define a standard order for the spin-orbital's indices in Eq. (2.1), including in the set only those simple products which contain no repeated indices and are ordered both with respect to them and to the arguments. This ensures that no two products will be present which differ only by a permutation of arguments, the same holding true for the derived OSP's. As two different spin orbitals may be obtained by taking the same orbitals with different spins, this means that the orbital part Φ, Eq. (2.11), may contain up to two identical orbitals.

If the atomic orbitals are normalized,

$$\|\varphi_j\|=1\ , \tag{2.15}$$

then so are all OSP's,

$$\|\Psi_p\|=1\ . \tag{2.16}$$

Both the OSP's and the AP's are in general not orthonormal, their metric matrices being

$$g_{pq}=\langle\Psi_p\,|\,\Psi_q\rangle\ , \tag{2.17}$$

$$A_{pq}=\langle f_p\,|\,f_q\rangle=\langle A\Psi_p\,|\,A\Psi_q\rangle=\langle\Psi_p\,|\,A\Psi_q\rangle\ , \tag{2.18}$$

where we have used Eqs. (2.4) and (2.5).

Any actual calculation deals with matrices and not with operators. This makes no difference for orthonormal basis because the representation of any operator equation is then faithful. As is discussed in Appendix, A, which is the reference for what follows, this is not the case when dealing with the nonorthonormal bases of our interest. In this case the matrix representation of the eigenvalue equation (2.7) reads

$$\underline{H}^f\underline{c} = E\underline{A}\,\underline{c}\ , \tag{2.19}$$

where $\underline{H}^f$ is the matrix representation of H in the basis $\{f_p\}$, and $\underline{c}$ is the column matrix of the coefficients in the expansion Eq. (2.9). Letting O be the orthonormalizer Eq. (A19) where f_p is here defined by Eq. (2.14), from $Af_p = f_p$ it follows that

$$OA = AO = O\ . \tag{2.20}$$

If we define the new Hermitian operator

$$G = O^\dagger HO\ , \tag{2.21}$$

$$G^\dagger = G\ , \tag{2.22}$$

then the results of Appendix A show that the matrix representation of the operator pseudoeigenvalue problem

$$Gv = EO^\dagger Ov \tag{2.23}$$

is given by the matrix eigenvalue equation

$$\underline{G}^f\underline{d} = \underline{E}\,\underline{d}\ . \tag{2.24}$$

Here, E is the molecular energy Eq. (2.7), and the molecular wave function Eq. (2.9) is given by

$$u = \sum_p c_p f_p = Ov = \sum_p (\underline{A}^{-1}\underline{O}\,\underline{d})_p f_p\ , \tag{2.25}$$

where $\underline{O}$ is the matrix representation of O in the basis $\{f_p\}$.

This is very convenient because one may then use all standard properties and techniques. If $\underline{G}^f$ is, for instance, a diagonal matrix, then its eigenvalues are the diagonal elements, a property which is not valid for Eq. (2.19).

Our goal is to go over from an eigenvalue problem in the space of the AP's to one in the space of the OSP's. While there is an isomorphism between the two sets given by the mapping Eq. (2.14), the OSP's cannot be expanded in terms of the AP's because a projection operator like A has no inverse. What we will do instead is to introduce a Hermitian equivalent Hamiltonian H_{eq} in the following way.

(1) The molecular energies are the eigenvalues of H_{eq},

$$H_{\text{eq}}u^{\text{eq}} = Eu^{\text{eq}},\ \ H_{\text{eq}}^\dagger = H_{\text{eq}}\ , \tag{2.26}$$

where

$$u^{\text{eq}} = \sum_p c_p^{\text{eq}}\Psi_p\ . \tag{2.27}$$

The matrix representation of Eq. (2.26) is then

$$\underline{H}\,{}^{\Psi}_{\text{eq}}\underline{c}^{\text{eq}} = E\underline{g}\,\underline{c}^{\text{eq}}\ . \tag{2.28}$$

(2) In order to have a proper matrix eigenvalue problem we define the new operator

$$G_{\text{eq}} = N^\dagger H_{\text{eq}}N,\ \ G_{\text{eq}}^\dagger = G_{\text{eq}}\ , \tag{2.29}$$

where N is the orthonormalizer of the OSP's. It then follows that

$$\underline{G}\,{}^{\Psi}_{\text{eq}}\underline{d}^{\text{eq}} = E\underline{d}^{\text{eq}}\ , \tag{2.30}$$

where

$$\underline{c}^{\text{eq}} = \underline{g}^{-1}\underline{N}\,\underline{d}^{\text{eq}}\ , \tag{2.31}$$

$\underline{N}$ being the matrix representation of N in the basis $\{\Psi_p\}$.

(3) We now define G_{eq} in such a way that the matrix eigenvalue problems Eqs. (2.24) and (2.30) are identical.[9] That is,

$$\underline{G}\,{}^{\Psi}_{\text{eq}} \equiv \underline{G}^f\ , \tag{2.32}$$

$$\underline{d}^{\text{eq}} = \underline{d}\ . \tag{2.33}$$

As G is a known operator, Eqs. (2.32) and (2.33) allows us to define H_{eq}, and to establish the connection between u^{eq} and u. We thus find

$$H_{\text{eq}} = (N^{-1})^\dagger G_{\text{eq}}N^{-1}\ , \tag{2.34}$$

where from Eq. (A29)

$$N^{-1} = \sum_{p,q} |\bar{\Psi}_p\rangle(\underline{g}\,\underline{N}^\dagger)_{pq}\langle\bar{\Psi}_q|\ , \tag{2.35}$$

$\{\bar{\Psi}_p\}$ being the basis biorthonormal to $\{\Psi_p\}$. We may therefore write [see Eq. (A9)]

$$H_{\text{eq}} = \sum_{p,q} |\bar{\Psi}_p\rangle(\underline{N}\,\underline{G}^f\underline{N}^\dagger)_{pq}\langle\bar{\Psi}_q| = M^\dagger HM\ , \tag{2.36}$$

where M is the mapping operator

$$M = \sum_{p,q} |f_p\rangle(\underline{A}^{-1}\underline{O}\,\underline{N}^\dagger)_{pq}\langle\bar{\Psi}_q|,\ \ M^\dagger = M^{-1}\ . \tag{2.37}$$

From $\underline{d}^{\text{eq}} = \underline{d}$, it immediately follows that

$$u = Mu_{\text{eq}}\ . \tag{2.38}$$

Summarizing, we have mimicked, in the space spanned by $\{\Psi_p\}$, the development leading from Eq. (2.7) to the eigenvalue equation (2.24) in the space spanned by $\{A\Psi_p\}$. The corresponding steps are given side by side in Table I, where we have also included those related to the establishment of a true matrix eigenvalue problem. The crucial equation is the definition Eq. (2.32).

If one wishes to obtain all the molecular eigenvalues and eigenfunctions, one needs only to solve the matrix eigenvalue equation (2.24). In order to write a model Hamiltonian H_{mod} operating in a model subspace corresponding to a reduced number of degrees of freedom—the spin ones in the example to be considered—it is necessary to go over to the operator eigenvalue equation (2.26). This comes about because the formulation of H_{mod} requires both a factorization of the wave function in the undesired degrees of freedom, and the use of the effective Hamiltonian formalism in order to define a new eigenvalue problem with the chosen dimension.

It is first of all necessary to define both an effective subspace Ω_{eff}, and a Hermitian reference Hamiltonian H_{ref} such that Ω_{eff} is spanned by one or several complete degenerate sets of eigenfunctions of H_{ref}. As in most cases of interest the effective Hamiltonian will be determined in a perturbative fashion, it is convenient to make the partition

TABLE I. Steps leading to the definition of H_{eq}. Each column corresponds to the space spanned by the basis at the heading. The actual line of reasoning goes down from the first equation of the third column, to the very bottom, and then up to the top of the second column.

$\{N\Psi_p\}$	$\{\Psi_p\}$	$\{A\Psi_p\}$	$\{OA\Psi_p\}$
	$H_{\text{eq}}u^{\text{eq}}=Eu^{\text{eq}}$	$Hu=Eu$	
	$u^{\text{eq}}=\sum_p c_p^{\text{eq}}\Psi_p$	$u=\sum_p c_pA\Psi_p$	
$\underline{H}_{\text{eq}}^{N\Psi}\underline{d}^{\text{eq}}=E\underline{d}^{\text{eq}}$	$\underline{H}_{\text{eq}}^{\Psi}\underline{c}^{\text{eq}}=E\underline{g}\,\underline{c}^{\text{eq}}$	$\underline{H}^{A\Psi}\underline{c}=E\underline{A}\,\underline{c}$	$\underline{H}^{OA\Psi}\underline{d}=E\underline{d}$
$\underline{H}_{\text{eq}}^{N\Psi}=\underline{G}_{\text{eq}}^{\Psi}$		$\underline{G}^{A\Psi}=\underline{H}^{OA\Psi}$	
	$G_{\text{eq}}=N^\dagger H_{\text{eq}}N$	$G=O^\dagger HO$	
	$\underline{G}_{\text{eq}}^{\Psi}\underline{d}^{\text{eq}}=E\underline{d}^{\text{eq}}$	$\underline{G}^{A\Psi}\underline{d}=E\underline{d}$	
	$\underline{c}^{\text{eq}}=\underline{g}^{-1}\underline{N}\,\underline{d}^{\text{eq}}$	$\underline{c}=\underline{A}^{-1}\underline{O}\,\underline{d}$	
	$\underline{G}_{\text{eq}}^{\Psi}=\underline{G}^{A\Psi}$		
	$\underline{d}^{\text{eq}}=\underline{d}$		

$$H_{\text{eq}}=H_{\text{ref}}+V \tag{2.39}$$

in such a way that V is small. From what was said in the Introduction,[10,11] V should therefore be related to the interatomic interaction.

Let the eigenfunctions of H_{ref} be

$$H_{\text{ref}}\Psi_p^{\text{ref}}=\epsilon_p\Psi_p^{\text{ref}} , \tag{2.40}$$

where

$$\langle \Psi_p^{\text{ref}} \mid \Psi_q^{\text{ref}}\rangle=\delta_{pq} . \tag{2.41}$$

The spectral decomposition of H_{ref} is then

$$H_{\text{ref}}=\sum_{\epsilon}\epsilon P_{\epsilon} , \tag{2.42}$$

where

$$P_{\epsilon}=\sum_{p\ (\epsilon_p=\epsilon)} \mid \Psi_p^{\text{ref}}\rangle\langle \Psi_p^{\text{ref}} \mid , \tag{2.43}$$

the last sum being over all degenerate eigenfunctions of H_{ref} with eigenvalue ϵ.

As is shown in Appendix B, the Hermitian effective Hamiltonian H_{eff} which represents H_{eq} in the subspace Ω_{eff} is given by the following expressions:

$$H_{\text{eff}}=S^\dagger H_{\text{eq}}S , \tag{2.44}$$

$$S=Z(Z^\dagger Z)^{-1/2} , \tag{2.45}$$

$$Z=P_0+X(Z\langle VZ\rangle-VZ)P_0 , \tag{2.46}$$

$$X=\sum_{\epsilon\ (\neq\epsilon_0)} P_{\epsilon}/(\epsilon-\epsilon_0) , \tag{2.47}$$

$$\langle VZ\rangle=\sum_{\epsilon}P_{\epsilon}VZP_{\epsilon} . \tag{2.48}$$

Here P_0 is the projection operator corresponding to the subspace Ω_{eff} spanned by the eigenfunctions of H_{ref} with eigenvalue ϵ_0. The eigenvalues E of H_{eq} stemming from ϵ_0 are given by the operator equation

$$H_{\text{eff}}w=Ew . \tag{2.49}$$

The corresponding eigenfunctions of H_{eq} are

$$u^{\text{eq}}=Sw , \tag{2.50}$$

so that the molecular wave function is given by

$$u=ASw . \tag{2.51}$$

Up to the second order of perturbation theory we obtain [see Eqs. (B18) and (B19)]

$$S=P_0-XVP_0 , \tag{2.52}$$

$$H_{\text{eff}}=P_0H_{\text{eq}}P_0-P_0XVP_0 , \tag{2.53}$$

an expression which will be used for the application discussed in Sec. III.

III. HEISENBERG'S MODEL HAMILTONIAN

A. The Heitler-London approximation

Disregarding magnetic interactions the H_2 molecular Hamiltonian in atomic units is given by[16]

$$H=H_0+U , \tag{3.1}$$

where

$$H_0=h_a(1)+h_b(2)+1/R , \tag{3.2}$$

$$U=-1/r_{1b}-1/r_{2a}+1/r_{12} , \tag{3.3}$$

h_a and h_b are the Hamiltonians of the isolated hydrogen atoms at $\mathbf{R}_a$ and $\mathbf{R}_b$, r_{1b} is the distance from electron 1 to nucleus b and similarly for r_{2a}, r_{12} is the interelectronic distance, and R the internuclear separation. We take as basis functions the OSP's generated by the ground-state orbitals of the constituent H atoms, which corresponds to the approximation of Heitler and London.[7,16] If $a_0(\mathbf{r}_1)$ and $b_0(\mathbf{r}_2)$ are the $1s$ hydrogen orbitals centered on $\mathbf{R}_a$ and $\mathbf{R}_b$, respectively, we get

$$\Psi_{0SM}=\Phi_0\chi_{SM},\quad S=0,1,\quad M=-S,-S+1,\ldots,S \tag{3.4}$$

$$\Phi_0=a_0(\mathbf{r}_1)b_0(\mathbf{r}_2) , \tag{3.5}$$

$$\begin{aligned}
&\chi_{00}=[\alpha(\sigma_1)\beta(\sigma_2)-\beta(\sigma_1)\alpha(\sigma_2)]/\sqrt{2} ,\\
&\chi_{11}=\alpha(\sigma_1)\alpha(\sigma_2) ,\\
&\chi_{10}=[\alpha(\sigma_1)\beta(\sigma_2)+\beta(\sigma_1)\alpha(\sigma_2)]/\sqrt{2} ,\\
&\chi_{1,-1}=\beta(\sigma_1)\beta(\alpha_2) .
\end{aligned} \tag{3.6}$$

It therefore follows that

$$H_0\Phi_0=\epsilon_0\Phi_0 , \tag{3.7}$$

where

$$\epsilon_0=2e_0+1/R , \tag{3.8}$$

and e_0 is the hydrogen atom's ground-state energy.

For the two-electron case the antisymmetrizer Eq. (2.3) is given by

$$A=(1-T_cT_s)/2\ , \tag{3.9}$$

where T_c and T_s are the coordinates' and spins' transposition operators, respectively. It is easily verified that the spinors χ_{SM} are eigenfunctions of T_s, so that

$$T_s\chi_{SM}=t_S\chi_{SM}\ , \tag{3.10}$$

where

$$t_1=1,\ \ t_0=-1\ , \tag{3.11}$$

from which one obtains

$$A\Psi_{0SM}=\tfrac{1}{2}(\Phi_0-t_ST_c\Phi_0)\chi_{SM}\ . \tag{3.12}$$

Notice that due to the choice Eq. (3.6) the wave functions Eq. (3.12) are, in general, linear combinations of Slater determinants.

The operator M_{sym}, Eq. (C21), may in our case be written

$$M_{\text{sym}}=A\,|\Phi_0\rangle A_{00}^{-1/2}(T_s)\langle\Phi_0|\ , \tag{3.13}$$

which from Eqs. (2.34), (3.7), (C18), and (3.5) gives

$$H_{\text{eq}}=|\Phi_0\rangle[\epsilon_0+\tfrac{1}{2}A_{00}^{-1/2}(T_s)(J-KT_s)A_{00}^{-1/2}(T_s)]\langle\Phi_0|\ . \tag{3.14}$$

Here we have used the commutation property

$$[A,H]=0\ , \tag{3.15}$$

which is a consequence of the fact that H is a symmetric operator.[15] Here we have not explicitly written the unit operator in spin space, $\sum_{S,M}|\chi_{S,M}\rangle\langle\chi_{S,M}|$. The Coulomb direct and exchange integrals are, respectively, given by

$$\begin{aligned} J&=J_{00}=\langle a_0b_0\,|\,Ua_0b_0\rangle\ ,\\ K&=K_{00}=\langle a_0b_0\,|\,Ub_0a_0\rangle\ . \end{aligned} \tag{3.16}$$

Upon writing

$$A_{00}^{-1}(T_s)=2/(1-Q^2T_s)=2(1+Q^2T_s)/(1-Q^4)\ , \tag{3.17}$$

where

$$Q=\langle a_0\,|\,b_0\rangle \tag{3.18}$$

is the usual overlap integral, it is immediately found that

$$\begin{aligned} H_{\text{eq}}=|\Phi_0\rangle[\epsilon_0&+(J-Q^2K)/(1-Q^4)\\ &-T_s(K-Q^2J)/(1-Q^4)]\langle\Phi_0|\ , \end{aligned} \tag{3.19}$$

which is the desired result.

As in this particular case the orbital part is fully factorized, it is possible to reduce H_{eq} to a spin-only Hamiltonian. Upon taking matrix elements with Φ_0, and bearing in mind that[17]

$$T_s=\tfrac{1}{2}+2\mathbf{s}_1\cdot\mathbf{s}_2\ , \tag{3.20}$$

we obtain the Heisenberg Hamiltonian

$$H_{\text{Heis}}=\langle\Phi_0\,|\,H_{\text{eq}}\Phi_0\rangle=E_0-2J_{\text{exch}}\mathbf{s}_1\cdot\mathbf{s}_2\ , \tag{3.21}$$

where

$$E_0=\epsilon_0+[(1+Q^2/2)J-(\tfrac{1}{2}+Q^2)K]/(1-Q^4)\ , \tag{3.22}$$

and

$$J_{\text{exch}}=(K-Q^2J)/(1-Q^4)\ . \tag{3.23}$$

It may be easily verified that E_0 is the baricenter of the energy eigenvalues, and that J_{exch} is half the separation between the singlet and triplet states. Heisbenberg Hamiltonians of this sort are usually obtained by comparing energies, no explicit connections being established between its eigenfunctions and the actual ones,[18,19] as has been done here.

While the Heitler-London approximation correctly gives the general features of the energy curve $E(R)$, the predicted equilibrium internuclear separation is 10% too large, and the dissociation energy is about $\frac{2}{3}$ of its actual value.[16] But its most drastic shortcoming is the fact that it predicts a singlet-triplet crossing at large distances[20,6] which is incompatible with the property of two-electron systems of always having a singlet ground state.[21] Any improvement on this situation requires introducing the excited states, as is discussed below.

B. The introduction of excited states

We now extend the previous basis in order to include excited eigenstates of the isolated neutral H atoms, disregarding the high-energy ionic states where two electrons are in the same atom (H^- ions). The OSP's Eqs. (C1) and (C2),

$$\Psi_p=\Phi_{j(S)}\chi_{SM}\ ,$$

$$\Phi_{jk}(\mathbf{r}_1,\mathbf{r}_2)=\varphi_j(\mathbf{r}_1)\varphi_k(\mathbf{r}_2)\ ,$$

are then such that the condition

$$j<k \tag{3.24}$$

is always fulfilled, because the case $j=k$ corresponds to the excluded ionic states. We will order the indices so that the first orbital in Eq. (C2) is centered on $\mathbf{R}_a$, and the second is centered on $\mathbf{R}_b$. As the set of allowed orbital parts $\{\Phi_j\}$ is the same for both values of S [see the discussion leading to Eqs. (C9) in Appendix C] we may therefore write

$$\Psi_p=\Phi_{jk}\chi_{SM}\ , \tag{3.25}$$

$$\Phi_{jk}=a_j(\mathbf{r}_1)b_k(\mathbf{r}_2)\ , \tag{3.26}$$

where j and k are now S independent, $\{a_j\}$ is an orthonormal set of atomic orbitals of the hydrogen atom centered at $\mathbf{R}_a$, and similarly for $\{b_k\}$. That is,

$$\begin{aligned} h_aa_j(\mathbf{r}_1)&=e_ja_j(\mathbf{r}_1)\ ,\\ h_bb_k(\mathbf{r}_2)&=e_kb_k(\mathbf{r}_2)\ . \end{aligned} \tag{3.27}$$

Taking into account Eqs. (3.26) and (3.27) it follows that

$$H_0\Phi_{jk}=\epsilon_{jk}\Phi_{jk},\ \ H_0\Psi_p=\epsilon_p\Psi_p\ , \tag{3.28}$$

$$\epsilon_{jk}=e_j+e_k+1/R\ ; \tag{3.29}$$

Due to the exclusion of the ionic states, it turns out that $\{\Phi_{jk}\}$ is an orthonormal set

$$\langle \Phi_{jk} \mid \Phi_{lm} \rangle = \langle a_j \mid a_l \rangle \langle b_k \mid b_m \rangle = \delta_{jl}\delta_{km} = \delta_{jk,lm} \ . \tag{3.30}$$

The symmetric mapping operator Eq. (C21) may now be simply written

$$M_{\text{sym}} = A \sum_{j,k} \mid \Phi_j \rangle A_{jk}^{-1/2}(T_s) \langle \Phi_k \mid \ , \tag{3.31}$$

where each subindex now stands for a pair of orbital indices.

From Eqs. (2.36) and (3.31) we obtain

$$\begin{aligned} H_{\text{eq}} &= M_{\text{sym}}^{\dagger} H M_{\text{sym}} \\ &= \sum_{j,k,l,m} \mid \Phi_j \rangle A_{jk}^{-1/2}(T_s) \langle \Phi_k \mid AHA\Phi_l \rangle \\ &\qquad \times A_{lm}^{-1/2}(T_s) \langle \Phi_m \mid \ , \end{aligned} \tag{3.32}$$

where each subindex stands for a pair of orbital subindices and we have used the Hermiticity of A. H being a symmetric operator it follows that[15]

$$[A,H] = 0 \ , \tag{3.33}$$

which from Eq. (2.5) gives

$$AHA = HA^2 = HA \ . \tag{3.34}$$

Upon defining the general direct and exchange Coulomb integrals

$$J_{jk} = \langle \Phi_j \mid U\Phi_k \rangle \ , \tag{3.35}$$

$$K_{jk} = \langle \Phi_j \mid UT_c\Phi_k \rangle \ , \tag{3.36}$$

the orbital matrix elements of H_{eq}, Eq. (3.32), may be written

$$\begin{aligned} \langle \Phi_j \mid H_{\text{eq}} \mid \Phi_m \rangle = \sum_k A_{jk}^{-1/2}(T_s) \epsilon_k A_{km}^{1/2}(T_s) \\ + \tfrac{1}{2} \sum_{k,l} A_{jk}^{-1/2}(T_s)(J_{kl} - K_{kl}T_s) \\ \times A_{lm}^{-1/2}(T_s) \ , \end{aligned} \tag{3.37}$$

which are spin operators. The previous expression reduces to Eq. (3.19) for the restricted basis Eq.(3.4).

In order to apply the effective Hamiltonian formalism we have to split H_{eq} into a known reference Hamiltonian H_{ref} and a remainder V. Because we intend to find H_{eff} in a perturbative fashion, V has to be small. Apart from the constant Coulomb nuclear interaction $1/R$, the first sum in Eq. (3.37) is essentially the isolated atoms' energy, and the second is the interatomic interaction. The last sum is therefore small compared with the first,[10,11] being a good candidate for V. Unfortunately the first term is not Hermitian, which is an unavoidable requisite for H_{ref}. We will instead take

$$H_{\text{ref}} = \sum_p \mid \Psi_p \rangle \epsilon_p \langle \Psi_p \mid \ , \tag{3.38}$$

which differs from the first sum in Eq. (3.37) only by terms of the order of Q^2 [Eq. (3.18)]. The spin matrices $\underline{H}_{\text{ref}}$ and $\underline{V}$ are therefore given by [see Eq. (2.39)]

$$\underline{H}_{\text{ref}} = \underline{\epsilon} \ , \tag{3.39}$$

$$\begin{aligned} \underline{V} = \underline{A}^{-1/2}(T_s)\underline{\epsilon}\,\underline{A}^{1/2}(T_s) - \underline{\epsilon} \\ + \tfrac{1}{2}\underline{A}^{-1/2}(T_s)(\underline{J} - \underline{K}T_s)\underline{A}^{-1/2}(T_s) \ . \end{aligned} \tag{3.40}$$

Presented in such a fashion the formalism correctly describes bond dissociation, a limit which is difficult to treat in most approaches.[22] We may now choose as the effective space the one corresponding to the Heitler-London approximation of Eqs. (3.4)–(3.6),

$$\Omega_{\text{eff}} = \{\Psi_{0SM} \mid S = 0,1, \ \ M = -S, -S+1, \ldots, S\} \ . \tag{3.41}$$

Up to the second order of perturbation theory we obtain [see Eqs. (B18) and (B19)]

$$S = P_0 - XVP_0 \ , \tag{3.42}$$

$$H_{\text{eff}} = P_0 H_{\text{eq}} P_0 - P_0 VXVP_0 \ . \tag{3.43}$$

The second terms in Eqs. (3.42) and (3.43) give the corrections to the Heitler-London model, which is thus shown to be the first-order approximation to H_{mod}. The spin-only Heisenberg Hamiltonian representing the spin dependence of the H_2 molecule ground state is now given by

$$H_{\text{Heis}} = \langle \Phi_0 \mid H_{\text{eff}} \Phi_0 \rangle = E_0 - 2J_{\text{exch}} \mathbf{s}_1 \cdot \mathbf{s}_2 \ , \tag{3.44}$$

where after some lengthy algebra it is shown in Appendix D that

$$E_0 = \Xi_{00} - \tfrac{1}{2}\Lambda_{00} \ , \tag{3.45}$$

$$J_{\text{exch}} = \Lambda_{00} \ , \tag{3.46}$$

where the matrices $\underline{\Xi}$ and $\underline{\Lambda}$ are defined in Appendix D. As we are here concerned only with the formalism, the numerical calculation of the contribution of the excited states to E_0 and J_{exch} will be reported elsewhere.

IV. CONCLUSIONS

We have established—through a linear mapping—an explicit connection between the actual molecular eigenvalue problem in the space of the antisymmetrized wave functions, and an equivalent problem in the space of suitably selected simple-product wave functions. The decoupling which the image eigenvalue problem makes possible provides a way of eliminating undesired electronic degrees of freedom. Thus, when using the effective Hamiltonian formalism in order to determine only a selected set of eigenvalues and eigenfunctions, it is possible to project out such unwanted degrees of freedom, if a simple condition is fulfilled. This condition, which has been previously discussed in connection with the decoupling of nonidentical particles,[3] is that the effective subspace given by the tensorial product of the subspaces of the desired and undesired degrees of freedom is such that the latter is one dimensional. It is then possible to explicitly write Hamiltonians which correspond to the model ones used in the interpretation of well-defined sets of experiments. In fact, the final goal of the present line of study is the calculation of the parameters appearing in the model Hamiltonians given by crystal-field theory.

The very abstract nature of the formalism made it necessary—both for the reader's convenience and in order to be sure that no essential detail was overlooked—to give an example simple enough to be given in a few pages, but having at the same time all the main complications. The H_2 molecule was chosen because it is known that in the first approximation the crystal-field Hamiltonian can be interpreted in terms of the superposition of central-ion–single-ligand interactions.[2] The exclusion of the ionic states was made only in order to simplify the algebra, but they will surely have to be taken into account in the actual numerical calculations. One should also notice that orders higher than the second have also to be considered in order to verify the convergence of the perturbative expansion. Herring (Ref. 6, p. 100) argues that many high-order contributions would be required to obtain good values of $J_{\rm exch}$ because of its strong dependence on the wave functions' tails. If such turns out to be the case, it might be convenient to use empirically adjusted model wave functions instead of the atomic ones, as is done for instance in the modified atoms-in-molecules method.[23]

The derivation of the Heisenberg Hamiltonian was chosen because it is the simplest example of a whole class of spin Hamiltonians widely used in the study of magnetic properties of solids. The necessary restriction of the nondegenerate nature of the ground orbital state makes the method applicable to the derivation of such spin Hamiltonians only for the case of insulators.

The extension to the many-electron and many-atom case seems fairly straightforward and will be made in a subsequent paper. In this case one unfortunately loses some nice properties of the two-electron system, such as the possibility of describing it exactly in terms of a spin metric operator. The spin Hamiltonian will in general contain other permutation operators apart from T_s, that is, products of more than two spin operators.[24]

In spite of the numerical complications introduced by the appearance of many-center integrals in the perturbative expansion, the authors believe that the formulation makes possible a first-principle interpretation of the parameters appearing in many commonly used model Hamiltonians.

APPENDIX A: NONORTHONORMAL BASIS

Let $\{f_j\}$ be a set of linearly independent nonorthonormal basis functions, their scalar products defining the elements of the metric matrix $\underline{g}$,

$$\underline{g}_{jk}=\langle f_j \,|\, f_k\rangle \, . \tag{A1}$$

This matrix is always Hermitian and positive definite,[25] the last property making it possible to define the positive-definite matrix $\underline{g}^n$, where n is any real number.[26]

The basis functions $\{\bar{f}_j\}$ biorthonormal to $\{f_j\}$ are uniquely defined from the condition

$$\langle \bar{f}_j \,|\, f_k\rangle=\langle f_j \,|\, \bar{f}_k\rangle=\delta_{jk} \, , \tag{A2}$$

where δ_{jk} is the Kronecker delta. It follows at once that

$$\bar{f}_j=\sum_k g_{kj}^{-1} f_k \, , \tag{A3}$$

$$f_k=\sum_l g_{lk}\bar{f}_l \, . \tag{A4}$$

In terms of biorthonormal functions an arbitrary linear operator A may be written

$$A=\sum_{l,m} |\bar{f}_l\rangle A_{lm}\langle \bar{f}_m| \, , \tag{A5}$$

where $\underline{A}$ is the matrix representation of A in the basis $\{f_j\}$ given by

$$A_{jk}=\langle f_j \,|\, Af_k\rangle \, . \tag{A6}$$

For instance, the unit operator is given by

$$\begin{aligned} 1_{\rm op} &= \sum_l |f_l\rangle\langle \bar{f}_l| = \sum_{l,m} |\bar{f}_l\rangle g_{lm}\langle \bar{f}_m| \\ &= \sum_l |\bar{f}_l\rangle\langle f_l| = \sum_{l,m} |f_l\rangle g_{lm}^{-1}\langle f_m| \, . \end{aligned} \tag{A7}$$

It is easily seen both from Eq. (A1) and the third member of Eq. (A7) that $\underline{g}$ is the matrix representation of the unit operator. The fact that this is not the unit matrix makes it necessary to review some preconceptions one has about matrix representations in nonorthonormal basis of operator equations such as

$$AB=C \, . \tag{A8}$$

Introducing the unit operator (A7) between A and B, and taking matrix elements in the basis $\{f_j\}$, we obtain

$$\underline{A}\,\underline{g}^{-1}\underline{B}=\underline{C} \, , \tag{A9}$$

thus showing that matrix representations in nonorthonormal basis are not faithful.

If, for instance, B is the inverse of A, so that Eq. (A8) may be rewritten

$$AB=1_{\rm op} \, , \tag{A10}$$

it then follows from Eq. (A9) that

$$\begin{aligned} A^{-1} &= \sum_{l,m} |\bar{f}_l\rangle(\underline{g}\,\underline{A}^{-1}\underline{g})_{lm}\langle \bar{f}_m| \\ &= \sum_{l,m} |f_l\rangle A_{lm}^{-1}\langle f_m| \, . \end{aligned} \tag{A11}$$

The eigenvalue equation

$$Hu=Eu \, , \tag{A12}$$

where

$$u=\sum_j c_j f_j \, , \tag{A13}$$

leads to the matrix equation

$$\underline{H}\,\underline{c}=E\underline{g}\,\underline{c} \, , \tag{A14}$$

where $\underline{c}$ is the column matrix of the coefficients c_j. In a nonorthonormal basis the matrix representation of an eigenvalue operator equation is not a standard eigenvalue problem. Equation (A14) may be rewritten as an eigenvalue equation but for an operator different from H. To realize how this may be done it is convenient to change to one of the infinitely many orthonormal basis $\{f'_j\}$ where

$$\langle f'_j \,|\, f'_k\rangle=\delta_{jk} \, , \tag{A15}$$

in which case we know the matrix representation to be faithful. Such a change of basis may be generated by an orthonormalization operator O defined by

$$f_j' = O f_j \ , \tag{A16}$$

and such that

$$\langle f_j' \mid f_k' \rangle = \langle O f_j \mid O f_k \rangle = \langle f_j \mid O^\dagger O f_k \rangle = \delta_{jk} \ . \tag{A17}$$

From Eq. (A9) its follows that

$$\underline{O}^\dagger \underline{g}^{-1} \underline{O} = \underline{1} \ , \tag{A18}$$

where $\underline{1}$ is the unit matrix.

The orthonormalizer O may be written

$$O = \sum_{l,m} \mid \bar{f}_l \rangle O_{lm} \langle \bar{f}_m \mid = \sum_{l,m} \mid f_l \rangle (\underline{g}^{-1} \underline{O}\, \underline{g}^{-1})_{lm} \langle f_m \mid \ , \tag{A19}$$

where O_{lm} is a matrix element in the basis $\{f_j\}$.

In order to avoid future misunderstandings it should be stressed that if one solely uses matrix representations in the basis $\{f_j\}$, then

$$O f_j \neq \sum_k O_{kj} f_k \ .$$

The reader will easily verify that one gets instead

$$O f_j = \sum_k O_{kj} \bar{f}_k = \sum_k (\underline{g}^{-1} \underline{O})_{kj} f_k \ . \tag{A20}$$

The general solution of Eq. (A18) is[25]

$$\underline{O} = \underline{g}^{1/2} \underline{U} \ , \tag{A21}$$

where $\underline{U}$ is any unitary matrix and $\underline{g}^{1/2}$ is chosen to be positive definite.

Upon expansion in the new basis of the eigenfunction u in Eq. (A9),

$$u = \sum_j c_j f_j = \sum_k c_k' f_k' \ , \tag{A22}$$

we get

$$\underline{c} = \underline{g}^{-1} \underline{O}\, \underline{c}' \ . \tag{A23}$$

Replacing Eq. (A23) into (A14), and taking into account that from Eq. (A18)

$$\underline{O}^{-1} = \underline{O}^\dagger \underline{g}^{-1} \ , \tag{A24}$$

we find

$$\underline{O}^\dagger \underline{g}^{-1} \underline{H}\, \underline{g}^{-1} \underline{O}\, \underline{c}' = E \underline{c}' \ , \tag{A25}$$

which is a standard eigenvalue equation. From Eqs. (A9) and (A18) we can see that Eq. (A25) is nothing but the matrix representation of the operator equation

$$O^\dagger H O u' = E O^\dagger O u' \ , \tag{A26}$$

where

$$u' = \sum_j c_j' f_j \ , \tag{A27}$$

and

$$u = O u' \ . \tag{A28}$$

From Eqs. (A11) and (A18), the inverse of the orthonormalizer has the following expression:

$$O^{-1} = \sum_{l,m} \mid \bar{f}_l \rangle (\underline{g}\, \underline{O}^\dagger)_{lm} \langle \bar{f}_m \mid \ . \tag{A29}$$

The particular choice

$$\underline{U} = \underline{1} \tag{A30}$$

leads to the symmetric orthonormalizer

$$\underline{O}_{\mathrm{sym}} = \underline{g}^{1/2} \ , \tag{A31}$$

$$\begin{aligned} O_{\mathrm{sym}} &= \sum_{l,m} \mid \bar{f}_l \rangle g_{lm}^{1/2} \langle \bar{f}_m \mid = \sum_{l,m} \mid \bar{f}_l \rangle g_{lm}^{-1/2} \langle f_m \mid \\ &= \sum_{l,m} \mid f_l \rangle g_{lm}^{-1/2} \langle \bar{f}_m \mid = \sum_{l,m} \mid f_l \rangle g_{lm}^{-3/2} \langle f_m \mid \ , \end{aligned} \tag{A32}$$

$$O_{\mathrm{sym}}^\dagger = O_{\mathrm{sym}} \ , \tag{A33}$$

but in the general case O is not Hermitian. The inverse operator Eq. (A29) is in this case expressed by

$$O_{\mathrm{sym}}^{-1} = \sum_{l,m} \mid \bar{f}_l \rangle g_{lm}^{3/2} \langle \bar{f}_m \mid \ . \tag{A34}$$

The symmetric orthonormalization is the simplest one which preserves the symmetry properties of the original basis functions.[27] This feature being of great importance when establishing the connection with model Hamiltonians, in actual calculations we will always use O_{sym}.

APPENDIX B: THE EFFECTIVE-HAMILTONIAN FORMALISM

Consider a physical system represented by a Hamiltonian H defined in an n-dimensional vectorial space Ω.

An effective Hamiltonian is the operator defined in the subspace Ω_{eff}, such that its eigenvalues and eigenfunctions are in a one-to-one correspondence with the chosen ones of H.

It is convenient to define a Hermitian reference Hamiltonian H_{ref} such that Ω_{eff} is spanned by the eigenfunctions belonging to one of its eigenvalues. H_{ref} does not have to represent an actual physical system: in the example given in the Introduction it would be the Hamiltonian of the free ion's valence electrons minus the spin-orbit interaction. Furthermore, Ω_{eff} could be spanned by the eigenfunctions belonging to several eigenvalues of H_{ref}, or a new new reference Hamiltonian could be defined which has the eigenvalue of interest the baricenter of the previous ones.

Let, therefore,

$$H_{\mathrm{ref}} \phi_{ja} = e_j \phi_{ja}, \quad a = 1, 2, \ldots, d_j \tag{B1}$$

where the second subindex distinguishes the different eigenfunctions belonging to the d_j-degenerate eigenvalue e_j. If e_j is the energy level determining Ω_{eff}, and

$$H \Psi_{ja} = E_{ja} \Psi_{ja} \ , \tag{B2}$$

then the levels E_{ja} of interest all stem from e_j, so that if

$$V = H - H_{\mathrm{ref}} \ , \tag{B3}$$

then

$$\Omega_{\text{eff}}=\{\phi_{ja} \mid a=1,2,\ldots,d_j\} , \tag{B4}$$

and

$$\lim_{V\to 0} E_{ja}=e_j . \tag{B5}$$

The effective Hamiltonian $\widetilde{H}_j$ is the operator such that

$$\widetilde{H}_j \widetilde{\Psi}_{ja}=E_{ja}\widetilde{\Psi}_{ja} , \tag{B6}$$

where

$$\widetilde{\Psi}_{ja}=\sum_{b=1}^{d_j} c_{ab}^{j}\phi_{jb} , \tag{B7}$$

$$\widetilde{H}_j=S_j^{-1}HS_j , \tag{B8}$$

$$\Psi_{ja}=S_j\widetilde{\Psi}_{ja} , \tag{B9}$$

S_j being the wave operator.

There is an infinity of nonsingular operators S_j satisfying Eqs. (B6)—(B9), the only restriction being that Ω_{eff} should be such that

$$P_j\Psi_{ja}\neq 0 \quad \text{for all } a , \tag{B10}$$

where

$$P_j=\sum_{a=1}^{d_j} |\phi_{ja}\rangle\langle\phi_{ja}| \tag{B11}$$

is the projection operator over Ω_{eff}. The simplest unitary wave operator S_j which yields a Hermitian effective Hamiltonian having the same symmetry properties as H is defined by[13]

$$S_j=Z_j(Z_j^{\dagger}Z_j)^{-1/2} , \tag{B12}$$

$$S_j^{-1}=S_j^{\dagger} , \tag{B13}$$

where Z_j satisfies the nonlinear equation

$$Z_j=P_j+X_j(Z_j\langle VZ_j\rangle-VZ_j)P_j , \tag{B14}$$

$$X_j=\sum_{k\,(\neq j)} P_j/(e_k-e_j) , \tag{B15}$$

and

$$\langle A\rangle=\sum_k P_kAP_k , \tag{B16}$$

with the limiting condition

$$\lim_{V\to 0} Z_j=P_j . \tag{B17}$$

Although Eq. (B14) may sometimes be solved exactly, one will most often solve it by iteration, whereupon one obtains the degenerate version of Rayleigh-Schrödinger perturbation theory. Up to second-order terms one gets[13,28]

$$S_j=P_j-X_jVP_j , \tag{B18}$$

$$\widetilde{H}_j=P_j(H-VX_jV)P_j=e_jP_j+P_jVP_j-P_jVX_jVP_j . \tag{B19}$$

In the perturbative approach it is essential to choose V in such a way that the higher-order terms are of decreasing magnitude, that is, to choose H_{ref} in such a way that it resembles H as much as possible.

APPENDIX C: THE TWO-ELECTRON CASE

We consider the two-electron case where the antisymmetrizer A is given by Eq. (3.9), and the orthonormal OSP's have the form

$$\Psi_p=\Phi_{jk}\chi_{SM},\quad \langle\Psi_p\mid\Psi_q\rangle=g_{pq}=\delta_{pq} , \tag{C1}$$

$$\Phi_{jk}(\mathbf{r}_1,\mathbf{r}_2)=\varphi_j(\mathbf{r}_1)\varphi_k(\mathbf{r}_2) . \tag{C2}$$

According to the discussion given in Sec. II on the choice of $\{\Psi_p\}$ it should be

$$j\leq k , \tag{C3}$$

and

$$A\Psi_p\neq 0 . \tag{C4}$$

It may be easily verified that

$$A=A_cS_s+S_cA_s , \tag{C5}$$

where A_c and S_c are the coordinates' antisymmetrizer and symmetrizer operators,[15] respectively, and similarly for the spins,

$$\begin{aligned} &A_j=(1-T_j)/2 ,\\ &S_j=(1+T_j)/2 , \end{aligned} \tag{C6}$$

where $j=c,s$. It follows at once from Eqs. (3.10) and (3.11) that

$$\begin{aligned} &A_s\chi_{00}=\chi_{00},\quad S_s\chi_{00}=0 ,\\ &A_s\chi_{1M}=0,\quad S_s\chi_{1M}=\chi_{1M} , \end{aligned} \tag{C7}$$

from which we obtain

$$\begin{aligned} &A\Psi_{jk00}=(S_c\Phi_{jk})\chi_{00} ,\\ &A\Psi_{jk1M}=(A_c\Phi_{jk})\chi_{1M} . \end{aligned} \tag{C8}$$

As it should be $A_c\Phi_{jk}\neq 0$, it follows that

$$\begin{aligned} &j\leq k \quad \text{if } S=0 ,\\ &j<k \quad \text{if } S=1 . \end{aligned} \tag{C9}$$

The metric matrix Eq. (2.18) is given by

$$\begin{aligned} A_{pq}&=\langle f_p\mid f_q\rangle=\langle A\Psi_p\mid A\Psi_q\rangle=\langle\Psi_p\mid A^{\dagger}A\Psi_q\rangle\\ &=\langle\Psi_p\mid A^2\Psi_q\rangle=\langle\Psi_p\mid A\Psi_q\rangle , \end{aligned} \tag{C10}$$

where we have used Eqs. (2.4) and (2.5). From Eqs. (C1), (3.10), and (2.12) it follows that

$$\begin{aligned} &A_{j(S)SM,k(S')S'M'}\\ &\quad=\langle\Phi_{j(S)}\mid\langle\chi_{SM}\mid \tfrac{1}{2}(1-T_cT_s)\chi_{S'M'}\rangle\mid\Phi_{k(S')}\rangle\\ &\quad=A_{j(S)k(S)}(t_S)\delta_{SS'}\delta_{MM'} , \end{aligned} \tag{C11}$$

where

$$A_{jk}(t)=\tfrac{1}{2}(\langle\Phi_j\mid\Phi_k\rangle-t\langle\Phi_j\mid T_c\Phi_k\rangle) \qquad \text{(C12)}$$

and each subindex now stands for a pair of indices.

The metric matrix is therefore block diagonalized, the two blocks corresponding to $S=0$ and $S=1$. As $\underline{\underline{A}}$ is positive definite, so are the aforementioned submatrices, upon which we obtain for any real n,

$$A^{n}_{j(S)SM,k(S')S'M'}=A^{n}_{j(S)k(S)}(t_s)\delta_{SS'}\delta_{MM'}\ , \qquad \text{(C13)}$$

where the powers $\underline{\underline{A}}^{n}$ may be obtained in the usual way.[26]

We discuss next the specialization of the symmetric orthonormalizer Eq. (A32) to the two-electron case:

$$\begin{aligned}O_{\mathrm{sym}}&=\sum_{l,m}A\mid\Psi_l\rangle A_{lm}^{-3/2}\langle\Psi_m\mid A=\sum_{S,S'}\sum_{M,M'}\sum_{j(S),k(S')}A\mid\Phi_{j(S)}\rangle\mid\chi_{SM}\rangle A^{-3/2}_{j(S)SM,k(S')S'M'}\langle\chi_{S'M'}\mid\langle\Phi_{k(S')}\mid A\\&=\sum_{S,j(S),k(S)}AP_S\mid\Phi_{j(S)}\rangle A^{-3/2}_{j(S)k(S)}(t_S)\langle\Phi_{k(S)}\mid P_SA\ ,\end{aligned} \qquad \text{(C14)}$$

where

$$P_S=\sum_M\mid\chi_{SM}\rangle\langle\chi_{SM}\mid=P_S^2=P_S^{\dagger}\ , \qquad \text{(C15)}$$

$$[P_S,A]=0\ , \qquad \text{(C16)}$$

and

$$P_0=A_s,\ \ P_1=S_s\ . \qquad \text{(C17)}$$

It is now convenient to define the spin operators

$$A_{jk}(T_s)=\langle\Phi_j\mid A\Phi_k\rangle=\tfrac{1}{2}(\langle\Phi_j\mid\Phi_k\rangle-\langle\Phi_j\mid T_c\Phi_k\rangle T_s) \qquad \text{(C18)}$$

such that

$$A_{jk}(T_s)\chi_{SM}=A_{jk}(t_S)\chi_{SM}\ , \qquad \text{(C19)}$$

as may be seen from Eq. (3.10). In what follows these operators will be called the metric spin operators.

It follows at once that Eq. (C14) may be written

$$O_{\mathrm{sym}}=A\sum_S P_S\sum_{j(S),k(S)}\mid\Phi_{j(S)}\rangle A^{-3/2}_{j(S)k(S)}(T_s)\langle\Phi_{k(S)}\mid P_SA\ . \qquad \text{(C20)}$$

The symmetric mapping operator Eq. (2.37) is therefore given by [see Eq. (A31)]

$$\begin{aligned}M_{\mathrm{sym}}&=O_{\mathrm{sym}}P_{\Psi}=A\sum_{l,m}\mid\Psi_l\rangle A_{lm}^{-1/2}\langle\Psi_m\mid\\&=A\sum_S P_S\sum_{j(S),k(S)}\mid\Phi_{j(S)}\rangle A^{-1/2}_{j(S)k(S)}(T_s)\langle\Phi_{k(S)}\mid P_S\ .\end{aligned} \qquad \text{(C21)}$$

APPENDIX D: SECOND-ORDER CORRECTIONS TO THE HEISENBERG HAMILTONIAN

Because T_s is an idempotent operator

$$T_s^2=T_s\ , \qquad \text{(D1)}$$

any matrix function $\underline{F}(T_s)$ may be written

$$\underline{F}(T_s)=\underline{F}_1+\underline{F}_2T_s\ , \qquad \text{(D2)}$$

where $\underline{F}_1$ and $\underline{F}_2$ are constant matrices. In particular Eq. (3.21) may be written

$$H_{\mathrm{Heis}}=\Xi_{00}-\Lambda_{00}T_s\ , \qquad \text{(D3)}$$

where $\underline{\underline{\Xi}}$ and $\underline{\Lambda}$ are matrices to be determined. The parameters E_0 and J_{exch} in Eq. (3.21) are then given by [see Eq. (3.20)]

$$E_0=\Xi_{00}-\tfrac{1}{2}\Lambda_{00}\ , \qquad \text{(D4)}$$

$$J_{\mathrm{exch}}=\Lambda_{00}\ . \qquad \text{(D5)}$$

In order to determine $\underline{\underline{\Xi}}$ and $\underline{\Lambda}$ we will use in the definition Eq. (3.21) the second-order approximation Eq. (2.53),

$$\underline{\underline{H}}_{\mathrm{eff}}=\underline{\underline{H}}_{\mathrm{eq}}-\underline{V}\,\underline{\underline{X}}\,\underline{V}\ , \qquad \text{(D6)}$$

where

$$\begin{aligned}\underline{\underline{H}}_{\mathrm{eq}}&=\underline{\underline{A}}^{-1/2}(T_s)\underline{\epsilon}\,\underline{\underline{A}}^{1/2}(T_s)\\&\quad+\tfrac{1}{2}\underline{\underline{A}}^{-1/2}(T_s)(\underline{J}-\underline{\underline{K}}T_s)\underline{\underline{A}}^{-1/2}(T_s)\ ,\end{aligned} \qquad \text{(D7)}$$

$$\underline{V}=\underline{\underline{H}}_{\mathrm{eq}}-\underline{\underline{H}}_{\mathrm{ref}}=\underline{\underline{H}}_{\mathrm{eq}}-\underline{\epsilon}\ . \qquad \text{(D8)}$$

From Eq. (D2) we may write

$$\underline{\underline{A}}^{1/2}(T_s)=\underline{\underline{\Delta}}+\underline{\Gamma}T_s\ , \qquad \text{(D9)}$$

$$\underline{\underline{A}}^{-1/2}(T_s)=\underline{\delta}+\underline{\gamma}T_s\ . \qquad \text{(D10)}$$

One could give explicit expressions of $\underline{\underline{\Delta}}$, $\underline{\Gamma}$, $\underline{\delta}$, and $\underline{\gamma}$ in terms of the matrix elements Eq. (2.18), but they are irrelevant for the discussion that follows. Introducing Eqs. (D9) and (D10) into (D7) we find

$$\underline{\underline{H}}_{\mathrm{eq}}=\underline{\underline{\Xi}}^{(1)}-\underline{\Lambda}^{(1)}T_s\ . \qquad \text{(D11)}$$

where

$$\underline{\underline{\Xi}}^{(1)}=\underline{\delta}\,\underline{\epsilon}\,\underline{\underline{\Delta}}+\underline{\gamma}\,\underline{\epsilon}\,\underline{\Gamma}+\tfrac{1}{2}(\underline{\delta}\,\underline{J}\,\underline{\delta}+\underline{\gamma}\,\underline{J}\,\underline{\gamma}-\underline{\delta}\,\underline{\underline{K}}\,\underline{\gamma}-\underline{\gamma}\,\underline{\underline{K}}\,\underline{\delta})\ , \qquad \text{(D12)}$$

$$\underline{\Lambda}^{(1)}=-\underline{\delta}\,\underline{\epsilon}\,\underline{\Gamma}-\underline{\gamma}\,\underline{\epsilon}\,\underline{\underline{\Delta}}+\tfrac{1}{2}(\underline{\delta}\,\underline{\underline{K}}\,\underline{\delta}+\underline{\gamma}\,\underline{\underline{K}}\,\underline{\gamma}-\underline{\delta}\,\underline{J}\,\underline{\gamma}-\underline{\gamma}\,\underline{J}\,\underline{\delta})\ , \qquad \text{(D13)}$$

the superscripts indicating that the given expressions are the first-order approximations. The reader may easily verify that, replacing Eqs. (D12) and (D13) into Eqs. (D4) and (D5), one may obtain the Heitler-London approximation Eqs. (3.22) and (3.23). The second-order corrections are obtained from the last term in Eq. (D6). Making use of Eqs. (D8) and (D11), it follows that

$$-\underline{V}\,\underline{\underline{X}}\,\underline{V}=\underline{\underline{\Xi}}^{(2)}-\underline{\Lambda}^{(2)}T_s\ , \qquad \text{(D14)}$$

where

$$\underline{\Xi}^{(2)}=-(\underline{\epsilon}-\underline{\Xi}^{(1)})\underline{X}(\underline{\epsilon}-\underline{\Xi}^{(1)})-\underline{\Delta}\,\underline{X}\,\underline{\Delta}\ , \tag{D15}$$

$$\underline{\Delta}^{(2)}=(\underline{\epsilon}-\underline{\Xi}^{(1)})\underline{X}\,\underline{\Delta}+\underline{\Delta}\,\underline{X}(\underline{\epsilon}-\underline{\Xi}^{(1)})\ . \tag{D16}$$

The parameters E_0 and J_{exch} may now be easily obtained from Eqs. (D4) and (D5), where

$$\underline{\Xi}=\underline{\Xi}^{(1)}+\underline{\Xi}^{(2)}\ , \tag{D17}$$

$$\underline{\Delta}=\underline{\Delta}^{(1)}+\underline{\Delta}^{(2)}\ . \tag{D18}$$

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina. Two of them (E.R.G. and G.A.A.) are obliged to the Bariloche Atomic Center for the kind hospitality which made the present work possible.

---

*To whom all correspondence should be addressed.

[1] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962).

[2] M. V. Eremin and A. A. Kornienko, Phys. Status Solidi B **79**, 775 (1977); D. J. Newman, J. Phys. F **13**, 1511 (1983).

[3] E. Dagotto and C. E. Solivérez, Phys. Rev. A **30**, 1616 (1984).

[4] K. W. H. Stevens, Phys. Rep. **24**, 1 (1976); B. H. Brandow, Adv. Phys. **26**, 651 (1977); N. Fuchikami and Y. Tanabe, J. Phys. Soc. Jpn. **45**, 1559 (1978).

[5] K. W. H. Stevens, in *Crystalline Electric Field and Structural Effects in f-Electron Systems,* edited by J. E. Crow, R. P. Guertin, and T. W. Mihalisin (Plenum, New York, 1980), p. 1.

[6] C. Herring, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. 2B, p. 1.

[7] W. Heitler and F. London, Z. Phys. **44**, 455 (1927).

[8] J. O. Hirschfelder, Chem. Phys. Lett. **1**, 363 (1967); **1**, 363 (1967); J. N. Murrell and G. Shaw, J. Chem. Phys. **46**, 1768 (1967).

[9] M. V. Eremin, A. A. Kornienko, and A. M. Leushin, Fiz. Tverd. Tela (Leningrad) **14**, 378 (1972) [Sov. Phys.—Solid State **14**, 314 (1972)].

[10] W. Moffitt, Proc. R. Soc. London, Ser. A **210**, 224 (1951).

[11] W. Moffitt, Proc. R. Soc. London, Ser. A **210**, 245 (1951).

[12] T. Arai, Phys. Rev. **134**, A824 (1964); Prog. Theor. Phys. **36**, 473 (1966).

[13] C. E. Solivérez, J. Phys. C **2**, 2161 (1969).

[14] C. E. Solivérez, Phys. Rev. A **24**, 4 (1981).

[15] A. Messiah, *Mécanique Quantique* (Dunod, Paris, 1962), Vol. II, pp. 504 and 505.

[16] M. Kotani, K. Ohno, and K. Kayama, in *Encyclopedia of Physics,* edited by J. Flügge (Springer, Berlin, 1961), Vol. XXXVII/2, p. 1.

[17] P. A. M. Dirac, *The Principles of Quantum Mechanics,* 4th ed. (Clarendon, Oxford, 1958), pp. 220—222.

[18] W. J. Caspers, Phys. **1**, 45 (1964).

[19] J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford, London, 1932), pp. 322—324; S. V. Vonsovskii, Magnetism (Wiley, New York, 1974), Vol. 2, pp. 554—559.

[20] C. Herring, Rev. Mod. Phys. **34**, 631 (1962).

[21] W. H. Kleiner and T. A. Kaplan, J. Math. Phys. **10**, 236 (1969).

[22] A. Goddard III, Phys. Rev. **157**, 81 (1967).

[23] G. G. Balint-Kurti and M. Karplus, in *Orbital Theories of Molecules and Solids,* edited by N. H. March (Clarendon, Oxford, 1974), p. 250.

[24] D. C. Mattis, *The Theory of Magnetism* (Harper and Row, New York, 1965), p. 88; S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum, New York, 1967), p. 56.

[25] P. O. Löwdin, Adv. Phys. **5**, 1 (1956).

[26] G. Goertzel and N. Tralli, *Some Mathematical Methods of Physics* (McGraw-Hill, New York, 1960), Chap. 2.

[27] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[28] C. E. Solivérez and E. Gagliano, Chem. Phys. Lett. **91**, 47 (1982).