Perturbation theory for intercenter electron exchange and superexchange with degeneracy

E. V. Orlenko and A. A. Rumyantsev

M. I. Kalinin Leningrad Polytechnical Institute

(Submitted 26 April 1989; after revision 9 October 1989)
Zh. Eksp. Teor. Fiz. **97**, 439–448 (February 1990)

Corrections to the energy and wave functions of a many-electron system of interacting atoms are evaluated in general analytic form, taking into account the degeneracy of states in accordance with the Young tableaux. The rule for writing down the perturbation operator for such systems is formulated in terms of the ground and excited state vectors that are antisymmetric in the interchange of electrons between centers. A perturbation theory in which one of the parameters is the degree of overlap of the wave functions is used to derive the secular equation of the theory. Examples of unpaired interatomic interactions due to exchange and superexchange effects are examined.

1. INTRODUCTION

Nonrelativistic mechanics makes extensive use of perturbation theory based on extrapolations such as the Rayleigh-Schrödinger series.[1] The theory then provides a basis for the description of a great variety of quantum phenomena on the atomic and molecular scale. Applications of this theory become less problematic in the context of the principle of indistinguishability of identical particles and the symmetrization (or antisymmetrization) requirement for the wave function of a set of interacting particles that follows from this principle.

It would seem that, for a system of electrons for which these requirements follow from the Pauli principle, they can be readily taken into account by applying the usual perturbation theory to the basis of unsymmetrized state, and using the antisymmetrization procedure *post factum* in each expansion term that determines the correction to the wave function in the particular perturbation-theory order. However, this procedure is unsatisfactory and can lead to results that are definitely incorrect. The point is that the perturbation operator used to construct the Rayleigh-Schrödinger series does not cover interactions due to the overlap of the wave functions of electrons belonging to different centers- ,nuclei, ions, or molecular cores. the way the perturbation is written down itself depends on the way the electrons are distributed over the centers. In the case of the ground-state energy correction for a multicenter molecular system, we immediately have a difficulty when the correction is evaluated as the matrix element between identical symmetrized states: the initial perturbation operator will also act on the "foreign" term in the wave function, and the distribution of electrons over the centers in the latter will require a change in the form of the perturbation operator. The resulting contradiction cannot be removed by the usual perturbation-theory techniques. Moreover, the theory does not even involve a parameter representing the overlap of the wave functions because exchange forces are not represented in the perturbation.

The features that we have just mentioned are also found to appear, and are simultaneously taken into account, in the vibrational procedure. For example, the exchange contributions are considered in the Heitler-London method and themselves contribute significantly to the perturbation over typical intermolecular separations. The method based on the "hybridization" of molecular orbitals is also found to demonstrate the importance of overlap and takes it into account correctly provided the initial or trial wave functions are suitably chosen. Variational methods are always based principally on intuition, and are used precisely when perturbation theory "does not work". This disadvantage is obviated when the perturbation theory is developed from first principles as a two-parameter formalism, i.e., when it contains a parameter that appears explicitly in the perturbation, and a further implicit parameter that represents the degree of intercenter overlap. A variant of this type of theory is described in Ref. 2; here, we consider the development of this theory and some new aspects of it that are associated with the degeneracy of states.

Exchange forces play a decisive part in the formation of valence bonds. The overlap of the electron shells of atoms in a molecule is responsible, in the final analysis, for the removal of the degeneracy in the spin states of electrons that correspond to different Young tableaux. The effect of total spin on energy splitting is indirect and is due to the symmetry of the wave functions, but the evaluation of this splitting can also be carried out by exchange perturbation theory (EPT). An analogous situation occurs when the effect of nuclear spin angular momenta on the energy states, or the terms of diatomic molecules such as oxygen (ground-state term $^3\Sigma_g{}^-$), is taken into account. This effect is unrelated to hyperfine interaction, and is entirely due to the particle interchange symmetry.[1] Exchange "selects" the energetically most appropriate of the nuclear Young tableaux.

Bashkin[2] has examined the ferro-or ferrimagnetism effect in a binary Boltzmann gas containing the light electron component. Here again, we can apparently use EPT to identify energetically most appropriate electron spin orientations.

The tendency in modern quantum physics is for phenomena determined by the multiparticle character of quantum interactions to become increasingly significant and topical. It is precisely in this direction that we must look for fundamental physical factors responsible for conceptual connections between processes occurring at radically different levels, i.e., atomic on the one hand and macroscopic on the other. The overlap of electron shells may be due to the interchange of electrons along a chain of atoms. This leads to

0038-5646/90/020244-05$03.00

quantum superexchange effects when the entire ensemble of atoms or molecules is involved in the interaction. It is clear that this type of effect is significant in the theory of ferromagnetism,[3,4] the theory of molecular chains (polymers), and in other phenomena due to multiparticle interactions.

We now briefly describe the situation encountered when a time-independent perturbation theory with exchange is constructed.[5] A number of difficulties arise when an attempt is made to construct a theory in which the corrections to wave functions are antisymmetrized with respect to the interchange of electrons. First, if the total Hamiltonian is symmetric with respect to the interchange of identical particles, subdividing it into perturbed and unperturbed parts means that the latter is antisymmetric because it is due to a particular distribution of labeled particles over the atoms. When the basis of eigenfunctions of this unperturbed Hamiltonian is employed, the corrections to these functions are found to be antisymmetric. On the other hand, if we use the basis of antisymmetric unperturbed wave functions, then we have the difficulty of having to orthogonalize the functions of this basis. A number of theoretical techniques, presented in the monograph of Ref. 6, employ a basis in which the excited-state vectors are not orthogonalized. The requirement of symmetrization is extended only to the eigenstates of the principal energy level. The theory then proceeds to a kind of compromise between different requirements, which is achieved by introducing the variational method at some stage of the calculations.

The variational stereotype was successfully overcome and a number of perturbation theories taking into account the symmetrization of states in all orders in the interaction parameters were constructed in Ref. 5. The procedure used to evaluate the expansion coefficients for the required functions in the unperturbed basis, which is described in Ref. 5, is also used in developing the EPT, and is therefore described below. The procedure is based on the use of projection operators in the space defined by the basis of symmetric states of a set of identical particles: $|\Psi\rangle = \hat{A}\,|\Psi)$, where $\hat{A}$ is the symmetrization operator.

2. FUNDAMENTALS OF EPT

The exchange interactions between closely spaced atoms involves the participation of outer-shell electrons of these atoms. These shells can include not only the outermost valence shell, but also inner shells adjacent to the last shell and providing an appreciable contribution to the overlap energy. For example, in the case of iron, the s and d shells with the maximum (equal to four) principal number must be regarded as outer shells. The overlap of d shells in solid iron is smaller than the s-shell overlap, but is responsible for the spin coordinate of atoms by exchange forces. In general, a total of $N > 2$ electrons will participate in the interaction of each pair of atoms.

We now turn to the two-center problem, i.e., the interaction between two atoms A and B separated by a distance R, and containing N_A and N_B electrons in the outer shells, so that $N = N_A + N_B$. The total antisymmetric wave function for the set of two atoms when their interaction is neglected can be written in the form of a simple product of atomic functions that include the spinor parts:

$$|\Phi_1) = \Psi_A(1,2,\dots,N_A)\,\Psi_B(N_A+1, N_A+2,\dots,N). \qquad (1)$$

where the subscript 1 of the state vector on the left-hand side represents a particular distribution of labeled electron over the atomic centers. For example, if we interchange electrons labeled 1 and $N_A + 1$ we obtain the state vector $|\Phi_2)$, and so on up to the vector $|\Phi_p)$, where p is the number of interchanges of electrons belonging to different atoms. The atomic wave functions describe the ground state of each of the atoms. At the same time, the spin angular momenta of atoms A and B are fixed, and each corresponds to a particular Young tableau. In other words, we shall assume that the procedure of symmetrization and alternation in the variables belonging to each of the atoms is complete. The combination of the Young tableaux for an atomic pair leads in general to r different Young tableaux for the pair as a whole. Each of the states labeled $\alpha = 1,2,\dots$ determines a particular value of the resultant spin of the atoms. If we neglect the interaction, all these states will have the same energy, which will be equal to the sum of the energies of the individual atoms. Degeneracy will be taken into account later. For the moment, let us consider one of the resultant Young tableaux for a paired set of atoms (for example, with $\alpha = 1$), assuming for the sake of simplicity that it is the only one.

To obtain the state vector for a paired set atoms that is antisymmetric in electron interchanges, we must form the algebraic sum of vectors $|\Phi_i)$ with allowance for the parities g_i of the interchanges and then multiply this sum by the normalizing factor f. We shall indicate this vector by an angle bracket:

$$|\Psi\rangle = \hat{A}\,|\Phi_1) = f\sum_{i=1}^{p}(-1)^{g_i}|\Phi_i), \qquad (2)$$

where, because of normalization,

$$\langle\Psi|\Psi\rangle = 1. \qquad (3)$$

Next,we define the operator representing projection onto the subspace of antisymmetric states by the relation

$$\Lambda_i|\Psi\rangle = |\Phi_i) \qquad (i=1,\ 2\dots \mathrm{p}) \qquad (4)$$

and take the Hamiltonian for the system in the form of the sum

$$\hat{H} = \hat{H}_0 + \hat{V}, \quad \hat{H}_0 = \sum_i \hat{H}_{0i}\Lambda_i, \quad \hat{V} = \sum_j \hat{V}_i\Lambda_i. \qquad (5)$$

where the subscript 0 labels the unperturbed Hamiltonian of the (isolated) system of atoms that has been made symmetric in electron interchanges, and the operator $\hat{V}$ is the similarly symmetrized perturbation operator. The operator $\hat{H}_{0i}$ is the unperturbed Hamiltonian corresponding to the distribution of electrons over the atoms for which the state of the atom that is unperturbed by the interaction is described by the state vector $|\Psi^0)$, where $\hat{V}_i$ is the perturbation operator for this distribution (labeled i).

In the absence of interaction between the atoms, the ground-state wave vector satisfies the equation

$$\hat{H}_0|\Psi^0\rangle = E^0|\Psi^0\rangle, \qquad (6)$$

which can be obtained by summing the Schrödinger equations for the states $|\Phi_i)$. If we suppose that the interaction is small, we can write the ground-state wave function and energy in the form of the following series:

$$|\Psi\rangle=|\Psi^0\rangle+|\Psi^1\rangle+\dots,\qquad E=E^0+E^1+\dots \tag{7}$$

In the first approximation in the perturbation, the Schrödinger equation takes the form

$$\hat{H}_0|\Psi^1\rangle+\hat{V}|\Psi^0\rangle=E^1|\Psi^0\rangle+E^0|\Psi^1\rangle. \tag{8}$$

The solution of this equation in the absence of degeneracy is obtained in Ref. 5, and is given by the following expressions:

$$|\Psi^1\rangle=\sum_b{}' \frac{\hat{P}|\Psi_b{}^0\rangle(\Phi_b|\hat{P}\hat{V}|\Psi_a{}^0\rangle}{pf_b(E^0-E_b{}^0)},\quad E^1=\langle\Psi^0|\hat{V}|\Psi^0\rangle,\quad \hat{P}=1-|\Psi\rangle(\Phi|/\langle\Psi|\Phi), \tag{9}$$

where $\hat{P}$ is the operator representing projection onto the subspace of vectors that is complementary to the ground-state vector. In the expression for the correction to the wave vector, the sum is evaluated over the excited states with energies E_0^b in the zeroth-order approximation. If we neglect the terms containing the overlap integrals, we find that the first two expressions in (9) become identical with the well known results obtained in the usual perturbation theory.

3. SECULAR EQUATION WITH EXCHANGE

If we take into account the degeneracy of the states of the atomic pair in the total spin (in accordance with the Young tableaux), we have to write the required state vector in the form of the following double sum:

$$|\Psi\rangle=\sum_{\alpha,n} c_{\alpha n}|\Psi_{\alpha n}{}^0\rangle,\quad c_{\alpha n}=c_\alpha{}^0\delta_{an}+c_{\alpha n}{}^1+\dots, \tag{10}$$

where the 0 indicates the state vector of the unperturbed system α is the number of one of the resulting Young tableaux and $n=a$, b are the subscripts of the corresponding ground (with energy $E_0=E_a^0$) and perturbed (with energy E_b^0) states. If we put $\alpha=1$, $n=a$, we obtain the unperturbed state vector used in the last section. In the first approximation we have instead of (8)

$$\sum_{\alpha,n}(E_n{}^0-E_a{}^0)c_{\alpha n}{}^1|\Psi_{\alpha n}{}^0\rangle=\sum_\beta c_{\beta a}{}^0(E_\beta{}^1-\hat{V})|\Psi_{\beta a}{}^0\rangle. \tag{11}$$

The usual method of reducing (11) to an algebraic system for the expansion coefficients, in which the equations undergo scalar multiplication by some unperturbed state vector, is now found to be unsatisfactory: the symmetrized state vectors with different indices are not orthogonal to one another. We therefore use a mathematical device that enables us to avoid this difficulty: we use the completeness of state vectors of the form $|\Phi)$, i.e.,

$$\sum_n|\Phi_{\alpha n})(\Phi_{\alpha n}|=1,\quad \sum_n|\Phi_{\alpha n}{}')(\Phi_{\alpha n}{}'|=1, \tag{12}$$

where the prime marks simple products of atomic state vectors that differ by the interchange of one of the electron pairs between the centers (see Sec. 2). The number of such interchanges and, correspondingly, the number of equations such as (12) is p for each fixed index α determining the type of Young tableau.

The above sums enable us to write the right-hand side of (11) in the form

$$\begin{aligned}(E^1-\hat{V})\sum_\beta c_{\beta a}{}^0|\Psi_{\beta a}{}^0\rangle &=\sum_{\alpha,n;\beta} p_\alpha{}^{-1}c_{\beta a}{}^0[|\Phi_{\alpha n})(\Phi_{\alpha n}|E^1-\hat{V}|\Psi_{\beta a}{}^0\rangle\\ &\quad+|\Phi_{\alpha n}{}')(\Phi_{\alpha n}{}'|E^1-\hat{V}|\Psi_{\beta a}{}^0\rangle+\dots]\\ &=\sum_{\alpha,n;\beta}(p_\alpha f_p)^{-1}c_{\beta a}{}^0|\Psi_{\alpha n}{}^0\rangle(\Phi_{\alpha n}|E^1-\hat{V}|\Psi_{\beta a}{}^0\rangle.\end{aligned} \tag{13}$$

The final result in (13) was obtained by a change of variables, by a reduction to integrals in the first term in brackets, and by using (2). We can now rewrite (11) in the form

$$\begin{aligned}\sum_{\alpha,n} c_{\alpha n}{}^1(E_n{}^0-E_a{}^0)|\Psi_{\alpha n}{}^0\rangle &=\sum_{\alpha,n;\beta}(p_\alpha f_p)^{-1}c_{\beta a}{}^0(\Phi_{\alpha n}|E^1-\hat{V}|\Psi_{\beta a}{}^0\rangle|\Psi_{\alpha n}{}^0\rangle\\ \Rightarrow\sum_{\alpha,n}\Big\{(E_n{}^0-E_a{}^0)c_{\alpha n}{}^1 &-\sum_\beta\frac{c_{\beta a}{}^0}{p_\alpha f_p}(\Phi_{\alpha n}|E^1-\hat{V}|\Psi_{\beta a}{}^0\rangle\Big\}|\Psi_{\alpha n}{}^0\rangle=0.\end{aligned} \tag{14}$$

Since the state vectors $|\Psi_{\alpha n}^0\rangle$ are linearly independent, the expression in braces in (14) must vanish for each pair of numbers α, n. In principle, this is then the solution to the problem of finding the expansion coefficients. In the first approximation, we have

$$(E_n{}^0-E_a{}^0)c_{\alpha n}{}^1=\sum_\beta\frac{c_{\beta a}{}^0}{p_\alpha f_p}(\Phi_{\alpha n}|E^1-\hat{V}|\Psi_{\beta a}{}^0\rangle. \tag{15}$$

Substituting $n=a$ in this expression, we obtain a homogeneous set of equations for the coefficients $c_{\beta a}^0=c_\beta$ that define the correct wave function in the zeroth-order approximation. By equating to zero the determinant of the system, we obtain the secular equation

$$\det(V_{\alpha\beta}-\Delta_{\alpha\beta}E^1)=0, \tag{16}$$

in which the matrix elements are given by

$$V_{\alpha\beta}=(\Phi_\alpha|\hat{V}|\Psi_\beta{}^0\rangle,\quad \Delta_{\alpha\beta}=(\Phi_\alpha|\Psi_\beta{}^0\rangle, \tag{17}$$

(the subscript a has been omitted). In contrast to the conventional formulation, the secular equation given above takes into account the intercenter overlap of the electron wave functions. When the vector $|\Psi\rangle$ is the product of coordinate and spin Young tableaux, we have $\Delta_{\alpha\beta}=\delta_{\alpha\beta}$ because of the orthogonality of the latter. This case will be examined later.

Next, we introduce the projection operator

$$\hat{P}_\gamma=\delta_\gamma-|\Psi_\gamma{}^0\rangle(\Phi_\gamma|/\Psi_\gamma{}^0|\Phi_\gamma], \tag{18}$$

where we have omitted the subscript a of the state vectors, and the operator δ_γ that acts on the superposition of vectors corresponding to different Young tableaux selects the term containing the subscript γ and retains only this term, in accordance with $\hat{P}_\gamma|\Psi_\gamma^0\rangle=0$. Applying the above operator to both sides of (11), we finally obtain the equation for the expansion coefficients in the first order:

$$\sum_{\alpha,n} (E_a{}^0-E_n{}^0)c_{\alpha n}{}^1\hat{P}_\gamma|\Psi_{\alpha n}{}^0\rangle=\sum_{\beta} c_\beta{}^0\hat{P}_\gamma\hat{V}|\Psi_\beta{}^0\rangle. \qquad (19)$$

The next step is based on the orthogonality and completeness of the basis of simple products $\Phi_{\alpha n}$, and is completely analogous to the derivation of (14). Equation (19) then assumes the form of the condition that the superposition of linearly independent antisymmetric states must be equal to zero. Applying the operator $\tilde{P}_\gamma$ to this superposition, using the idempotency property $\tilde{P}_\gamma^2=\tilde{P}_\gamma$ of the projection operator, and equating to zero the expansion coefficients in front of the linearly independent vectors, we obtain the following relation for the required corrections to the state characterized by the subscripts γ, a:

$$\overset{1}{c}_{\alpha n,\gamma a}=\sum_{\beta}\frac{(\Phi_{\alpha n}|\hat{P}_a\hat{V}|\Psi_{\beta a}{}^0\rangle}{pf_p(E_a{}^0-E_n{}^0)}, \qquad (20)$$

where $n\neq a$ in the sum on the right-hand side. If we neglect overlap, this becomes identical with the well known expression obtained in the usual perturbation theory. To verify this, we must insert the sum $\hat{P}$, $\hat{V}$ between the operators $\Sigma|\Phi_m)(\Phi_m|$. The term with $n=a$ in (20) will then vanish identically, and the terms containing the second component of (18) will also vanish for $m\neq a$. The result is that only the terms containing the matrix elements of the form

$$(\Phi_{\alpha n}|\hat{V}_1|\Phi_{\beta a})\equiv V_{\alpha n,\,\beta a},$$

will remain in the final expression, where $\hat{V}_i$ is the antisymmetrized perturbation operator introduced in Sec. 2.

4. INTERCENTER SUPEREXCHANGE

The fluorides of transition metals, such as MnF_2, exhibit the property of antiferromagnetism at sufficiently low temperatures. The crystal structure of these compounds is such that the magnetic interactions involve nearest-neighbor atoms lying at the corners of an equilateral triangle with the anions F^- occupying two of the corners and the cation Mn^{2+} occupying the third. The valence shall of the fluorine ion is similar to that of neon, and the valence shell of manganese have five electrons with unpaired spins.

The exchange interaction in MnF^2 crystal cannot be explained in terms of ordinary exchange between manganese ions because of the presence of another element between the ions (in this case, fluorine). The antiferromagnetic ordering of electron spins belonging to the manganese ions can be explained in terms of the perturbation theory in the Young tableaux.

Let us now consider an arbitrary pair of electrons with opposite spins in the outer shell of the fluorine ion. We label them 1 and 4. Next we take one electron from each of the d shells in the manganese ions that are closest to the fluorine, and label then 2 and 3. Finally, we consider spin Young tableaux of two types (see Fig. 1). The coordinate parts of the wave vectors are described by analogous schemes, with the rows and columns interchanged.

We use $\varphi(i)$, $\psi(i)$, $\tilde{\psi}(i)$ to denote the coordinate parts of one-electron wave functions of the ith electron that refer, respectively to the fluorine ion and the manganese ions lying on either side of the former. The coordinate part of the total state wave vector, described by the Young tableaux a (see Fig. 1) has the form

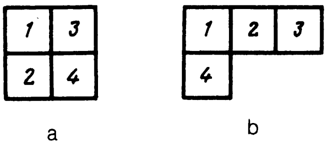

FIG. 1.

$$\begin{aligned}\Psi=f\{&\varphi(1)\varphi(4)\psi(2)\tilde{\psi}(3)-\varphi(1)\varphi(2)\psi(4)\tilde{\psi}(3)\\&+\varphi(1)\varphi(3)\psi(2)\tilde{\psi}(4)\\&-\varphi(3)\varphi(4)\psi(2)\tilde{\psi}(1)+\varphi(2)\varphi(4)\psi(1)\tilde{\psi}(3)+\ldots\},\end{aligned} \qquad (21)$$

where f is the normalizing coefficient and the expression in braces gives the explicit terms representing only the pair interchanges. The ellipsis represents negligible contributions that account for the interchanges of a large number of electrons, and also the interchanges of electrons belonging to the manganese ions. The exchange contributions corresponding to these terms in the interaction energy are very small because they result from the multiple overlap of the wave functions of electrons belonging to different centers, or because these centers are far apart. We must now also write down the spin part of the state vector for this diagram. In the usual notation, we have

$$\chi={}^1/_2(\alpha_1\beta_2-\alpha_2\beta_1)(\alpha_3\beta_4-\alpha_4\beta_3). \qquad (22)$$

The interaction operator includes the usual Coulomb terms representing the interaction between electrons belonging to "foreign" centers, the energy of attraction to these centers, and the repulsion energy between the ionic centers. This operator is obviously symmetric in the interchange of any of the interacting electron pairs.

The matrix element V_{aa} (for $n=a$) that corresponds to diagram a contains a direct contribution to the interaction energy that is independent of the spin direction, and also an exchange contribution that depends significantly on the overlap of the wave functions and is different for different orientations of the electrons spins in the system. It is precisely these exchange contributions that finally determine which mutual orientation of the spin angular momenta of the electrons is energetically appropriate. It will therefore be sufficient to confine our attention to this kind of contribution. Since the interchange terms in the function given by (21) have alternating signs, and, as already noted, the interaction operator is invariant under the pair interchanges, the corresponding exchange contributions to V_{aa} in this sum is found to be zero. It may be said that the exchange energy is zero for states described by Young tableaux of type a (see Fig. 1). The spins and, consequently, the magnetic moments of electrons belonging to the manganese ions have opposite directions in pairs, which corresponds to the antiferromagnetic state of the lattice.

If we now turn to the Young tableaux of type b (see figure), we find that, in contrast to (21), the interchange terms in the coordinate part of the state vector all have the positive sign. This behavior is typical for equally directed spins. In accordance with the Heitler-Landau method, the overlap of wave functions leads in this case of a higher energy of the system, i.e., $V_{bb}>V_{aa}$, and numerical estimates confirm this. The off-diagonal matrix element is $V_{ab}=0$ because of the readily proved orthogonality of spin vectors corresponding to different Young diagrams.

The exchange energy for the other Young tableaux is also found to be higher, which is readily verified. This means that the antiferromagnetic state does indeed occur in crystal lattices of this type. The effect of superexchange in the intercenter interaction produces a reduction in the energy of the state with mutually correlated spins.

We emphasize in conclusion that none of this demands an evaluation of corrections to the energy of the system in second-order perturbation theory when the intermediate excited states[3] are considered because the entire energy-lowering effect is essentially already present in the first-order terms of the usual perturbation theory.

APPENDIX

Projection operator

The antisymmetrized function for the system is the simple product of the state functions of the individual atoms

$$\Phi_0 \doteq \Psi_{0A}(r_1, \ldots, r_k)\,\Psi_{0B}(r_{k+1}, \ldots, r_N)$$

and is the eigenfunction of the unperturbed Hamiltonian with the corresponding distribution of electrons in atoms in A and B, i.e., $\hat{H}_{00}\Phi_0 = E_0\Phi_0$, where

$$\hat{H}_{00} = -\sum_{i=1}^{N}\frac{1}{2}\nabla_i^2 - \sum_{i=1}^{k}\frac{1}{r_{Ai}} - \sum_{i=k+1}^{N}\frac{1}{r_{Bi}} + \sum_{i=1}^{k}\sum_{j=k+1}^{N}\frac{1}{r_{ij}}.$$

The function Φ_1 in which electrons numbered 1 and $k+1$ have been interchanged is also an eigenfunction of the operator H_{01} with the same interchange, i.e., we can write out the following set of equations:

$$\hat{H}_{00}\Phi_0 = E_0\Phi_0,$$
$$\hat{H}_{01}\Phi_1 = E_0\Phi_1,$$
$$\cdot\ \cdot\ \cdot\ \cdot\ \cdot$$

We now label these equations so that, on the right, we obtain the function corresponding to the coordinate part of the Young tableaux for which the symmetrization procedure is being carried out:

$$|\Psi^0\rangle = \sum_i (-1)^{P_i}|\Phi_i).$$

The result is

$$\sum_i (-1)^{P_i}(\hat{H}_{0i} - E_0)|\Phi_i) = 0. \tag{A1}$$

We now introduce the operator $\lambda_i = |\Phi_i)(\Phi_i|$:

$$\hat{\lambda}_i|\Psi^0\rangle = |\Phi_i)\left(1 + \sum_{j\neq i}(-1)^{P_j}S_j\right),$$

where $S_j = (\Phi_i|\Phi_j)$, so that

$$|\Phi_i) = \hat{\lambda}_i|\Psi^0\rangle\left(1 + \sum_j (-1)^{P_j}S_j\right)^{-1}. \tag{A2}$$

Substituting (A2) in (A1), we obtain

$$\sum_i \hat{H}_{0i}|\Phi_i) = E_0|\Psi^0\rangle.$$

If we put

$$\hat{\lambda}_i\left(1 + \sum_{j\neq i}(-1)^{P_j}S_j\right)^{-1}$$

we obtain the following equations for the symmetrized function, which we have used as the starting point of our analysis:

$$\sum_i \hat{H}_{0i}\Lambda_i|\Psi^0\rangle = E^0|\Psi^0\rangle$$

or $\hat{H}_0|\Psi_2\rangle = E^0|\Psi^2\rangle$, where

$$\hat{H}_0 = \sum_i \hat{H}_{0i}\Lambda_i.$$

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Translated by S. Chomet