EXCHANGE EFFECTS IN THE DEGENERATE PERTURBATION THEORY OF INTERMOLECULAR POTENTIALS

by

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ABSTRACT

The contribution of electron exchange to intermolecular potentials is studied using the operator form of perturbation theory, when the non-interacting system of atoms or molecules is degenerate. A general, symmetry adapted degenerate perturbation theory is developed, including the almost-degeneracy case. Perturbation expansions are given up to second order in the energy. Differential equations for the perturbed wavefunctions are obtained, as well as their associated variational principles.

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I. Introduction

When dealing with the interaction of atoms or molecules, for example in collision processes or inside crystals, the wavefunctions and energies for the non interacting system are sometimes accurately known, in which case it is convenient to use perturbation theory to obtain the corrections due to the interaction. Furthermore, the new wavefunctions are required to have a symmetry corresponding to an irreducible representations of the group of the full hamiltonian. This symmetry is usually imposed by applying a group theoretical projection operator $\mathcal{A}$, for the appropriate representation, to the set of unperturbed states. But a set of linearly independent unperturbed wavefunctions may become linearly dependent after being projected, so that the development of a perturbation theory in terms of the eigenstates for the non interacting system requires special attention.

This problem is present in the perturbation theory of intermolecular potentials in the intermediate range between long distances, where a multipole expansion is used and exchange effects neglected, and short distances, where chemical binding is found and the exchange effects predominate. Here the operator $\mathcal{A}$ antisymmetrizes the total wavefunction with respect to electron exchange.

The perturbation theory of intermolecular potentials including exchange was initiated by Eisenschitz and London[1] and continued since then by several authors[2-8]. The use of linearly dependent basis sets has led sometimes to inconsistencies in the literature, which have been avoided more recently[9-12] by using linearly independent, usually orthonormalized, sets.

Another fruitful approach[13,14] has been based on operator perturbation theory,[15,16] which helps to isolate the difficulties derived from the symmetry problem[17]. In this contribution we want to use the operator approach to study the problem when the non interacting system is degenerate. For example, degeneracy will exist if the non interacting atoms or molecules have orbital degeneracy or their spins coupled to a multiplicity smaller than the highest. We shall keep these examples in mind but develop the formalism in general.

In section II we give the basic equations for symmetry adapted, degenerate perturbation theory and consider also the almost-degeneracy case. Section III includes the perturbation expansions when the degeneracy is completely removed in first order and when it persists to first order and is removed to second order. Section IV gives the corresponding differential equations and discusses their associated variational principles.

II. Symmetry adapted, degenerate perturbation theory

Let us consider a system of atoms or molecules whose energy E_0 in the absence of interactions is g times degenerate, with the unperturbed states given by $\{\varphi_{0i}\}$, $g \geq i \geq 1$. This set of linearly independent, non-symmetrized wavefunctions will form, together with the set of excited states $\{\varphi_k\}$, $k > g$, which verifies $\langle \varphi_k | \varphi_{oi} \rangle = 0$, a complete basis to describe the non-interacting system.

We want to obtain a perturbative solution for the interacting system in terms of this complete basis, including the symmetry properties of the whole system. Indicating with $\mathcal{A}$ the group theoretical projection operator which selects the wavefunction components belonging to the irreducible representation of interest, it will in general be a product of a point group projection operator times the antisymmetry projection operator. The set of symmetry adapted states $\{\mathcal{A}\varphi_{oi}\}$ is not necessarily linearly independent and could lead to ill behaved expansions. In order to avoid this difficulty we introduce the g x g overlap matrix (or Gram's matrix) $\underset{\sim}{A}$ for the set,

$$\underset{\sim}{A} = [\langle \varphi_{oi} | \mathcal{A} | \varphi_{oj} \rangle] \ , \tag{1}$$

which is hermitian, and diagonalize it by means of the unitary transformation $\underset{\sim}{S}$ to obtain the diagonal matrix $\underset{\sim}{\alpha}$,

$$\underset{\sim}{S}^{\dagger} \underset{\sim}{A} \underset{\sim}{S} = \underset{\sim}{\alpha} \tag{2}$$

The eigenvalues α_i of $\underset{\sim}{A}$ are definite positive, i.e. $\alpha_i \geq 0$, and we indicate the corresponding eigenvectors, the i-th columns of $\underset{\sim}{S}$, by $\underset{\sim}{S}_i$, so that

$$\underset{\sim}{A} \underset{\sim}{S}_i = \alpha_i \underset{\sim}{S}_i \ . \tag{3}$$

Selecting the $h \leq g$ eigenvectors with eigenvalues different from zero we form the states

$$\Psi_{op} = \alpha_p^{-\frac{1}{2}} \sum_i S_{ip} \mathcal{A} \varphi_{oi} = \alpha_p^{-\frac{1}{2}} \mathcal{A} \underset{\sim}{\varphi_o} \underset{\sim}{S}_p \tag{4}$$

where $h \geq p \geq 1$ and $\underset{\sim}{\varphi_o}$ is a row matrix with elements φ_{oi} . These states form a set of symmetry adapted, linearly independent wavefunctions describing the non-interacting system of atoms or molecules. In effect, clearly $\mathcal{A}\Psi_{op} = \Psi_{op}$, and

$$\begin{aligned} \langle \Psi_{op} | \Psi_{oq} \rangle &= (\alpha_p \alpha_q)^{-\frac{1}{2}} \sum_{ij} S_{ip}^{*} S_{jq} \langle \varphi_{oi} | \mathcal{A} | \varphi_{oj} \rangle \\ &= (\alpha_p \alpha_q)^{-\frac{1}{2}} (\underset{\sim}{S}^{\dagger} \underset{\sim}{A} \underset{\sim}{S})_{pq} = \alpha_{pq} (\alpha_p \alpha_q)^{-\frac{1}{2}} = \delta_{pq} \end{aligned} \tag{5}$$

so that they are orthonormalized. Notice that this result is obtained without imposing the orthonormality of the set $\{\varphi_{oi}\}$.

We shall use the previous results to set up the eigenvalue problem using the wave and reaction operator formalism[16], indicating with capital greek letters the symmetrized states, and introducing the projection operators

$$\mathcal{O}_p = |\Psi_{op}\rangle\langle\Psi_{op}| \quad , \mathcal{O} = \sum_p \mathcal{O}_p \quad) \tag{6}$$

and

$$\mathcal{P} = \mathcal{A} - \mathcal{O} \ . \tag{7}$$

In Schrödinger equation $(H-E)\Psi = 0$, $\langle \Psi | \Psi \rangle = 1$, we have $\mathcal{A}\Psi = \Psi$ and $[H, \mathcal{A}] = 0$, so that only the projection with $\mathcal{A}$ will give a right hand side different from zero and we can write, in the usual way,

$$\mathcal{O}(H-E)\mathcal{O}\Psi + \mathcal{O}(H-E)\mathcal{P}\Psi = 0 \ , \tag{8.a}$$

$$\mathcal{P}(H-E)\mathcal{O}\Psi + \mathcal{P}(H-E)\mathcal{P}\Psi = 0 \ . \tag{8.b}$$

From (8.b) we obtain

$$\mathcal{P}\Psi = TH\mathcal{O}\Psi \ , \quad T = \mathcal{P}[\alpha(1-\mathcal{A}) + \beta\mathcal{O} + \mathcal{P}(E-H)\mathcal{P}]^{-1}\mathcal{P} \tag{9}$$

where α and β insure that T is well defined and do not affect the results, and replacing (9) in (8.a),

$$\mathcal{O}(H-E)W\mathcal{O}\Psi = 0 \ , \quad W = \mathcal{O} + TH \ . \tag{10}$$

Introducing the notation

$$\mathcal{O}\Psi = \sum_p \Psi_{op} \langle \Psi_{op} | \Psi \rangle = \sum_p c_p \Psi_{op} \tag{11}$$

and projecting the first Eq. (10) on $\langle \Psi_{op'}|$, we obtain the secular equation

$$\sum_{p} \left(\langle \Psi_{op'} | HW | \Psi_{op} \rangle - E_q \, \delta_{p'p} \right) c_{qp} = 0 , \qquad (12)$$

discussed in detail by Löwdin for $\mathcal{A} = 1$. Here the index $h \geq q \geq 1$ numbers the energies that split from E_0 due to the interaction, and we have used the result $\langle \Psi_{op'} | W | \Psi_{op} \rangle = \langle \Psi_{op'} | \mathcal{O} | \Psi_{op} \rangle = \delta_{p'p}$. Once the coefficients c_{qp} are known the states Ψ_q corresponding to E_q are obtained from (9),

$$\Psi_q = \mathcal{O}\Psi_q + \mathcal{P}\Psi_q = \sum_{p} c_{qp} (1 + TH) \Psi_{op} \; . \qquad (13)$$

Equations (12) and (13) may be rewritten explicitly in terms of the unsymmetrized states

$$\psi_{op} = \alpha_p^{-\frac{1}{2}} \sum_{i} S_{ip} \, \varphi_{oi} \qquad (14)$$

using the decomposition $H = H_0 + V$, to obtain the secular determinant

$$\det \left[\langle \psi_{op'} | V\mathcal{A} | \psi_{op} \rangle + \langle \psi_{op'} | VTV | \psi_{op} \rangle - (E_q - E_0^{(0)}) \, \delta_{p'p} \right] = 0$$

$$(15)$$

For $i = p = 1$ we put $\varphi_{01} = \varphi_0$, $\alpha_1 = \langle \varphi_0 | \mathcal{A} | \varphi_0 \rangle$, and re-obtain Van der Avoird's result for the non-degenerate case. For $h = g$, i.e., when the set $\{\mathcal{A}\varphi_{0i}\}$ is linearly independent, the full $\underset{\sim}{S}$ unitary transformation appears in (15), which can then be eliminated to obtain, in matrix notation,

$$\det\left[\langle \underset{\sim}{\varphi_0} | V \mathcal{A} | \underset{\sim}{\varphi_0} \rangle + \langle \underset{\sim}{\varphi_0} | VTV | \underset{\sim}{\varphi_0} \rangle - (E_q - E_0^{(0)}) \underset{\sim}{A} \right] = 0 \tag{16}$$

If the matrix elements of second and higher order in V are neglected in (16) we are left with the valence bond secular equation usually obtained when the interacting system wavefunction is written as a projected linear combination of Slater determinants constructed from the products φ_{0i} of isolated atom wavefunctions[18].

It is seen from eq. (12) that we can always choose

$$\sum_p c^*_{q'p} c_{qp} = N_q \delta_{q'q} \tag{17}$$

and using (13) ,

$$\langle \Psi_{q'} | \Psi_q \rangle = N_q \delta_{q'q} + \sum_{pp'} c^*_{q'p'} c_{qp} \langle \psi_{0p'} | V T^2 V | \psi_{0p} \rangle \tag{18}$$

Equation (12) together with $\langle \Psi_q | \Psi_q \rangle = 1$ will then determine the coefficients c_{qp} , $h \geq p \geq 1$, uniquely or alternatively, choosing N_q will determine the norm of Ψ_q . It is also seen from Eq. (18) that for fixed c_{qp} values the states Ψ_q are orthogonal within an error of second order in V. In the following section we shall find it convenient to use the condition

$$\sum_p c_{qp}^{(0)*} c_{qp} = 1 \tag{19}$$

where the $c_{qp}^{(0)}$ are obtained from the lowest order solution of Eq. (12).

In some cases the unperturbed state of interest will not be degenerate, but its energy will be close to other unperturbed energy levels, their difference being small compared with the magnitude of the interaction. This situation may arise when dealing, for example, with spin-orbit effects. These almost degenerate cases can be treated in the way described above[19]. Let us indicate with $E_i^{(0)}$ and φ_{0i}, $g \geqslant i \geqslant 1$, the closely spaced energies and their wavefunctions and let φ_k, $k > g$, indicate the other unperturbed states. We introduce the operator Δ defined by

$$\Delta = \sum_i \Delta_i |\varphi_{0i}\rangle\langle\varphi_{0i}| \tag{20a}$$

$$\Delta_i = \frac{1}{g}\left(\sum_{j=1}^{g} E_j^{(0)}\right) - E_i^{(0)} = E_{Av}^{(0)} - E_i^{(0)} \tag{20b}$$

and write

$$H = H_0 + V = (H_0 + \Delta) + (V - \Delta) = \overline{H}_0 + \overline{V}\,. \tag{21}$$

We find then that

$$\overline{H}_0 \varphi_{0i} = E^{(0)}_{Av} \varphi_{0i} \quad , \quad g \geqslant i \geqslant 1 \ , \tag{22}$$

so that $E^{(0)}_{Av}$ is g times degenerate and $\{\varphi_{0i}\}$ is a g-order degenerate set. The previous and following results may then be applied to these problems by simply replacing E_0 , H_0 and V by $E^{(0)}_{Av}$, $\overline{H}_0$ and $\overline{V}$ respectively.

III. Perturbation expansion in the operator formalism

To obtain the eigenfunction Ψ_q and eigenvalue E_q of the interacting system of atoms or molecules to increasing order in the potential V , we require a perturbation expansion for T . This we shall do, following Van der Avoird's treatment[14], by noticing that

$$\mathcal{P}(E-H) = (E^{(0)}_0 - H_0)\mathcal{A} - \Lambda V'\mathcal{A} \tag{1}$$

where Λ is a normal, idempotent operator defined by

$$\Lambda = 1 - \sum_{p} |\Psi_{0p}\rangle\langle\psi_{0p}| \ , \tag{2}$$

which verifies $\mathcal{P} = \Lambda\mathcal{A} = \mathcal{A}\Lambda^{+}$, and where

$$V' = V - (E - E^{(0)}_0) \ . \tag{3}$$

From (1) and the defining equation for T ,

$$\mathcal{P}(E-H)T = (E_0^{(0)}-H_0)T - \Lambda V'T = \mathcal{P} . \tag{4}$$

Introducing the unsymmetrized resolvent operator

$$R_0 = \sum_{k>g} (E_0^{(0)}-E_k^{(0)})^{-1} |\varphi_k\rangle\langle\varphi_k| \tag{5}$$

satisfying

$$\mathcal{P}R_0(E_0^{(0)}-H_0)\mathcal{P} = \mathcal{P} \tag{6}$$

and operating with $\mathcal{P}R_0$ to the left of (4), we get

$$T = \mathcal{P}R_0\mathcal{P} + \mathcal{P}R_0\Lambda V'T \tag{7}$$

Using the relation

$$\mathcal{P}R_0\Lambda V'\mathcal{P}R_0\mathcal{P} = \mathcal{P}R_0\mathcal{P}V'\Lambda^{\dagger}R_0\mathcal{P} \tag{8}$$

and iterating in Eq. (7) it is found that, provided the iteration expansion converges, $T = T^{\dagger}$. The hermitian character of T may be explicitly shown by replacing T in the right hand side of (7) by $T^{\dagger}$, so that

$$\begin{aligned} T &= \mathcal{P}R_0\mathcal{P} + \mathcal{P}R_0\Lambda V'\mathcal{P}R_0\mathcal{P} + \mathcal{P}R_0\Lambda V'TV'\Lambda^{\dagger}R_0\mathcal{P} \\ &= \mathcal{P}R_0\mathcal{P} + \mathcal{P}R_0\Lambda\tfrac{1}{2}(V'\mathcal{A}+\mathcal{A}V')\Lambda^{\dagger}R_0\mathcal{P} + \mathcal{P}R_0\Lambda V'TV'\Lambda^{\dagger}R_0\mathcal{P} \end{aligned} \tag{9}$$

In this form T may be expanded as a sum of hermitian terms, which may be obtained in the basis set of unsymmetrized states for the non-interacting system.

To calculate Ψ_q and E_q we must solve by iteration the equations

$$\sum_p \left[\langle\psi_{op'}|V\mathcal{A}|\psi_{op}\rangle + \langle\psi_{op'}|VTV|\psi_{op}\rangle - (E_q - E_0^{(0)})\delta_{p'p}\right] c_{qp} = 0 \tag{10a}$$

and

$$\mathcal{P}\Psi_q = TV\sum_p c_{qp}\psi_{op} = TV\varphi_q \, . \tag{10b}$$

The procedure to follow will depend on the degeneracy being completely or partially removed, or persistent in first order, or second order, etc. We shall only consider two cases:

I. The degeneracy is completely removed in first order.

II. It is persistent to first order but completely removed to second order.

Other cases may be dealt with in similar ways.

We start with case I. To first order we get from Eq. (10a)

$$\sum_p \left(\langle\psi_{op'}|V\mathcal{A}|\psi_{op}\rangle - E_q^{(1)}\delta_{p'p}\right) c_{qp}^{(0)} = 0 \tag{11}$$

which gives h different eigenenergies $E_q^{(1)}$ and, choosing

$$\sum_p c^{(0)*}_{q'p} c^{(0)}_{qp} = \delta_{q'q} , \tag{12}$$

the unsymmetrized states $\varphi^{(0)}_q = \sum_p c^{(0)}_{qp} \psi_{0p}$ and $\Psi^{(0)}_q = \mathcal{A} \varphi^{(0)}_q$. Replacing $\varphi^{(0)}_q$ in (10b) we get

$$\mathcal{P}\Psi^{(1)}_q = \mathcal{P} R_0 \mathcal{P} V \varphi^{(0)}_q \tag{13}$$

and using

$$\mathcal{P} V \varphi^{(0)}_q = \mathcal{A} \Delta^{+} V \varphi^{(0)}_q = \mathcal{A} \, (V - E^{(1)}_q) \, \varphi^{(0)}_q \tag{14}$$

the result is

$$\mathcal{P}\Psi^{(1)}_q = \mathcal{P} R_0 \mathcal{A} \, (V - E^{(1)}_q) \, \varphi^{(0)}_q \, . \tag{15}$$

To obtain the coefficients $c^{(1)}_{qp}$ required in $\mathcal{O}\Psi^{(1)}_q$, as well as the second order energy $E^{(2)}_q$, we proceed to the second order approximation for (10a), given by

$$\langle \psi_{0p'} | V \mathcal{P} \Psi^{(1)}_q \rangle + \sum_p \left(\langle \psi_{0p'} | V \mathcal{A} | \psi_{0p} \rangle - E^{(1)}_q \delta_{p'p} \right) c^{(1)}_{qp}$$

$$- E^{(2)}_q \, c^{(0)}_{qp'} = 0 \tag{16}$$

Multiplying by $c_{q'p'}^{(0)*}$, summing over p' and using Eq. (11) and (13),

$$\langle \varphi_{q'}^{(0)} | V \mathcal{P} R_0 \mathcal{P} V | \varphi_q^{(0)} \rangle + (E_{q'}^{(1)} - E_q^{(1)}) \sum_p c_{q'p}^{(0)*} c_{qp}^{(1)} - E_q^{(2)} \delta_{q'q} = 0 \tag{17}$$

so that for $q' = q$,

$$E_q^{(2)} = \langle \varphi_q^{(0)} | (V - E_q^{(1)}) \mathcal{A} R_0 \mathcal{A} (V - E_q^{(1)}) | \varphi_q^{(0)} \rangle . \tag{18}$$

To find $c_{qp}^{(1)}$ we write

$$\varphi_q^{(1)} = \sum_{q'} \gamma_{qq'}^{(1)} \varphi_{q'}^{(0)} \qquad \text{or} \qquad c_{qq''}^{(1)} = \sum_{q'} \gamma_{qq'}^{(1)} c_{q'q''}^{(0)} \tag{19}$$

and replacing the second expression in Eq. (17) we get, for $q' \neq q$,

$$\gamma_{qq'}^{(1)} = (E_q^{(1)} - E_{q'}^{(1)})^{-1} \langle \varphi_{q'}^{(0)} | (V - E_q^{(1)}) \mathcal{A} R_0 \mathcal{A} (V - E_q^{(1)}) | \varphi_q^{(0)} \rangle \tag{20}$$

which together with $\gamma_{qq}^{(1)} = 0$, resulting from $\sum c_{qp}^{(0)*} \times c_{qp}^{(1)} = 0$, define $\mathcal{O}\Psi_q^{(1)} = \mathcal{A}\varphi_q^{(1)}$. We also obtain from Eq. (10b),

$$\mathcal{P}\Psi_q^{(2)} = \mathcal{P}R_0\mathcal{P}V\varphi_q^{(1)}$$

$$+ \mathcal{P}R_0\Delta\frac{1}{2}\left[(V-E_q^{(1)})\mathcal{A}+\mathcal{A}(V-E_q^{(1)})\right]\Delta^{+}R_0\mathcal{A}(V-E_q^{(1)})\varphi_q^{(0)} \qquad (21)$$

This procedure may be continued to obtain higher order results. For example, the third order energy will be given by

$$E_q^{(3)} = \langle\varphi_q^{(0)}|(V-E_q^{(1)})\mathcal{A}R_0$$

$$\times\Delta\frac{1}{2}\left[(V-E_q^{(1)})\mathcal{A}+\mathcal{A}(V-E_q^{(1)})\right]\Delta^{+}R_0\mathcal{A}(V-E_q^{(1)})|\varphi_q^{(0)}\rangle$$

$$+\sum_{q'\neq q}(E_q^{(1)}-E_{q'}^{(1)})^{-1}\left|\langle\varphi_q^{(0)}|(V-E_q^{(1)})\mathcal{A}R_0\mathcal{A}(V-E_q^{(1)})|\varphi_q^{(0)}\rangle\right|^2 \qquad (22)$$

In case II we would get, from the solution of equation (11), $E_q^{(1)} = E_{q'}^{(1)}$, for $h \geq q, q' \geq 1$, and the $\varphi_q^{(0)}$ states would be yet undetermined up to an unitary transformation. We go then to the second order approximation to Eq. (10a) and write

$$\sum_p\left(\langle\psi_{0p'}|V\mathcal{P}R_0\mathcal{P}V|\psi_{0p}\rangle - E_q^{(0,2)}\delta_{p'p}\right)c_{qp}^{(0,0)}$$

$$+\sum_p\left(\langle\psi_{0p'}|V\mathcal{A}|\psi_{0p}\rangle - E_q^{(1)}\delta_{p'p}\right)c_{qp}^{(0,1)} = 0 \qquad (23)$$

Putting

$$c^{(0,0)}_{qp} = \sum_{q''} d^{(0)}_{qq''} c^{(0)}_{q''p} \quad , \tag{24}$$

multiplying Eq. (23) by $c^{(0)*}_{q'p'}$, and summing over p' we obtain, after using Eq. (11),

$$\sum_{q''} \left(\langle \varphi^{(0)}_{q'} | V \mathcal{P} R_0 \mathcal{P} V | \varphi^{(0)}_{q''} \rangle - E^{(0,2)}_{q} \delta_{q'q''} \right) d^{(0)}_{qq''} = 0 \tag{25}$$

which gives us h different second order energies $E^{(0,2)}_{q}$,

$$\varphi^{(0,0)}_{q} = \sum_{p} c^{(0,0)}_{qp} \psi_{0p} = \sum_{q'} d^{(0)}_{qq'} \varphi^{(0)}_{q'} \tag{26}$$

and $\Psi^{(0,0)}_{q} = \mathcal{A} \varphi^{(0,0)}_{q}$. We also obtain from Eq. (10b),

$$\mathcal{P} \Psi^{(0,1)}_{q} = \mathcal{P} R_0 \mathcal{P} V \varphi^{(0,0)}_{q} \tag{27}$$

To find $c^{(0,1)}_{qp}$ and $E^{(0,3)}_{q}$ we would go to the next order, as done in case I, and so on.

This completes our discussion of the perturbative solutions. To compute second order energies we would need to perform sums over the excited states of H_0 , included in R_0 . When dealing with corrections to ground state energies, it will be useful in some cases to use the inequality[16]

$$0 > R_0 > (E_0^{(0)} - E_{g+1}^{(0)}) \sum_{k=g+1}^{\infty} |\varphi_k\rangle\langle\varphi_k| \tag{28}$$

from which the following bounds are obtained for $E_q^{(2)}$,

$$0 > E_q^{(2)} > (E_0^{(0)} - E_{g+1}^{(0)}) \langle \varphi_q^{(0)} | (V - E_q^{(1)}) \mathcal{A} \sum_{i=1}^{g} |\varphi_{0i}\rangle\langle\varphi_{0i}|$$

$$\times \mathcal{A} (V - E_q^{(1)}) | \varphi_q^{(0)} \rangle . \tag{29}$$

The Unsöld approximation may be considered as an interpolation between these two bounds.

IV. Differential Equations and Variational Principles.

In connection with practical applications, it is frequently useful to work with the differential equations for each perturbation order and their associated variational principles^{20}.

To obtain a differential equation we shall look for a wavefunction χ belonging to the total (unsymmetrized) space, such that

$$\mathcal{P}\Psi = \mathcal{P}\chi . \tag{1}$$

From the relation

$$T = T^{(0)} + T^{(0)} V' T \tag{2.a}$$

$$T^{(0)} = \mathcal{P} [\alpha (1 - \mathcal{A}) + \beta \mathcal{O} + \mathcal{P} (E_0^{(0)} - H_0) \mathcal{P}]^{-1} \mathcal{P} \tag{2.b}$$

and (III.10b) we get, introducing $\mathcal{Q} = 1 - \mathcal{P}$

$$\chi_q = T^{(0)} V \varphi_q + T^{(0)} V_q' \mathcal{P} \chi_q + \mathcal{Q} \chi_q \,, \tag{3}$$

and operating to the left with $\mathcal{P}\ (E_0^{(0)} - H_0)$,

$$\mathcal{P}(E_0^{(0)} - H_0) \chi_q = \mathcal{P} V \varphi_q + \mathcal{P} V_q' \Lambda^{+} \chi_q \,. \tag{4}$$

Rather than working with this equation we may try to solve the "related" equation

$$(E_0^{(0)} - H_0) \chi_q = \mathcal{P} V \varphi_q + \mathcal{P} V_q' \Lambda^{+} \chi_q \tag{5}$$

and, since this χ_q would also solve Eq. (4), we can write $\mathcal{P}\Psi_q = \mathcal{P}\chi_q$. The normalization condition for Ψ_q requires that $\langle \chi_q | \mathcal{P} | \chi_q \rangle$ be finite. Otherwise we are free to choose, to solve Eq. (5), the boundary condition $\langle \varphi_{0i} | \chi_q \rangle = 0$, $q \geq i \geq 1$. It is then seen that the formal solution

$$\begin{aligned} \chi_q &= R_0 \mathcal{P} V \varphi_q + R_0 \mathcal{P} V_q' \Lambda^{+} \chi_q \\ &= (1 - R_0 \mathcal{P} V_q' \Lambda^{+})^{-1} R_0 \mathcal{P} V \varphi_q \end{aligned} \tag{6}$$

gives, after expanding and rearranging terms, a solution for $\mathcal{P}\Psi_q$ identical to the one obtained in Section III. Equation (5) together with the adjoint related equation

$$(E_0^{(0)} - H_0)\chi_q^a = \mathcal{P} V \varphi_q + \Lambda V_q' \mathcal{P} \chi_q^a \tag{7}$$

may be obtained from the variation function

$$J_q[\tilde{\chi}_q, \tilde{\chi}_q^a] = \langle \varphi_q | \varphi_q \rangle^{-1} (\langle \tilde{\chi}_q^a | \mathcal{P} V | \varphi_q \rangle$$

$$+ \langle \varphi_q | V \mathcal{P} | \tilde{\chi}_q \rangle - \langle \tilde{\chi}_q^a | E_0^{(0)} - H_0 - \mathcal{P} V_q' \Lambda^{\dagger} | \tilde{\chi}_q \rangle) \tag{8}$$

where $\langle \varphi_{0i} | \tilde{\chi}_q \rangle = \langle \varphi_{0i} | \tilde{\chi}_q^a \rangle, \; g \geq i \geq 1$,

and the variational principle

$$\delta J_q / \delta \tilde{\chi}_q = \delta J_q / \delta \tilde{\chi}_q^a = 0 \tag{9}$$

It is seen from Eq. (8) that in order to get χ_q and χ_q^a it is necessary to solve first the secular equation (III.10a), to obtain E_q and φ_q . This may be done using again a perturbation treatment. Once $E_q^{(1)}$ and $\varphi_q^{(0)}$ are known from the solution of Eq. (III.11) one would obtain $\chi_q^{(1)}$ from the first order approximation to Eq. (5),

$$(E_0^{(0)} - H_0)\chi_q^{(1)} = \mathcal{P} V \varphi_q^{(0)} \tag{10}$$

for case I of the previous section. A variational expression for $\chi_q^{(1)}$ may also be found expanding $J_q = \sum_{n=0}^{\infty} J_q^{(n)}$ and noticing that $J_q^{(0)} = J_q^{(1)} = 0$. Since Eq. (10) does not include the non-hermitian operator Δ^+, it will be $\tilde{\chi}_q^{(1)} = \tilde{\chi}_q^{a(1)}$ and $J_q^{(2)}$ may be written

$$J_q^{(2)}[\tilde{\chi}_q^{(1)}] = \langle \tilde{\chi}_q^{(1)} | \mathcal{P} V | \varphi_q^{(0)} \rangle + \langle \varphi_q^{(0)} | V \mathcal{P} | \tilde{\chi}_q^{(1)} \rangle - \langle \tilde{\chi}_q^{(1)} | E_0^{(0)} - H_0 | \tilde{\chi}_q^{(1)} \rangle \qquad (11)$$

where we have used $\langle \varphi_q^{(0)} | \varphi_q^{(0)} \rangle = 1$. Equation (11) is a symmetry adapted Hylleraas variational principle[21].[*] Variational principles for higher orders and for case II may be discussed along the same lines[22].

Variational principles of the Hylleraas type, like Eq. (11), are useful provided the solution to the zeroth order problem is accurately known. When this is not so it will be usually more convenient to use the full variational principle. It is also seen that charge transfer effects may be studied by incorporating in Eq. (11) the corresponding charge transfer states. Nevertheless, that may complicate the computation of the last term in Eq. (11), making

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[*] Putting $\tilde{\chi}_q^{(1)} = \chi_q^{(1)} + \delta \tilde{\chi}_q^{(1)}$ in this equation it is found that $J_q^{(2)}[\tilde{\chi}_q^{(1)}] \geq J_q^{(2)}[\chi_q^{(1)}] = E_q^{(2)}$, so that (11) leads to a minimum variational problem for $\tilde{E}_q^{(2)} = J_q^{(2)}[\tilde{\chi}_q^{(1)}]$.

again more convenient to use the full variational principle. The best computational method to follow should be chosen in accordance with each particular problem.

V. Discussion

In the previous treatment we have assumed that the solution for the non-interacting system of atoms or molecules is accurately known. This will certainly be the case when dealing with interacting hydrogen atoms. The equations obtained for the energies and wave-functions may be used to describe a pair of hydrogen atoms in a symmetry state corresponding to excited, i.e. orbitally degenerate, non-interacting hydrogens, or to describe more than two hydrogen atoms in a state with multiplicity smaller than the highest. For other atoms the usefulness of the perturbation approach with depend on the accuracy of the unperturbed states.

As it is usually the case with perturbation theoretical treatments, we have assumed that the iteration solution of the equations converges, in which case the energy has been shown to be real to all orders. With respect to the meaning of "order" in symmetrized perturbation theory it may be useful to take into account that the zero order problem is recovered by taking $V \to 0$ and $\mathcal{A} \to 1$. For example, when dealing with Eq. (IV.5) we can write

$$\mathcal{P} V' \Lambda^{+} = \mathcal{P}(H-E)\Lambda^{+} - \mathcal{P}(H_0 - E_0^{(0)})\Lambda^{+}$$

$$= \mathcal{P}(H_0 - E_0^{(0)})(\mathcal{P}-1) + \mathcal{P} V' \mathcal{P}$$

where in the right hand side we apparently have a zeroth order term. Nevertheless, for $\mathcal{A} \rightarrow 1$ the operator $\mathcal{P}$ commutes with $H_0 - E_0^{(0)}$ and the term disappears in the unperturbed problem. Consequently, the whole expression must be considered as a first order one.

From the knowledge of Ψ_{f} accurate to a certain order it is possible to compute expectation values of properties of the interacting system to the same order. The applicability of Dalgarno's interchange theorem for expectation values is restricted as in unsymmetrized degenerate perturbation theory[20]. This restriction might have been expected, since our results reduce to those of unsymmetrized degenerate perturbation theory for $\mathcal{A} = 1$.

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