

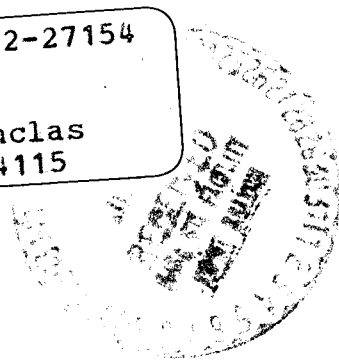
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ON OPTIMIZING THE TREATMENT OF EXCHANGE PERTURBATIONS †

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ABSTRACT

In a practical treatment of exchange perturbation problems one seeks the best wavefunction of the form $\Psi(1) = A(\phi_0 + \phi_1)$ where A is a symmetry projection operator, ϕ_0 is the eigenfunction of the unperturbed Hamiltonian, H_0 , and ϕ_1 is the solution to a first order perturbation equation of the form $(H_0 - E_0)\phi_1 + (V - E_1)\phi_0 = (1 - A)F_1$. Most previous treatments correspond to assuming that $F_1 = \sum_{\nu, j} v_{A, \nu j} (v_{\alpha_j} + v_{\beta_j} V)\phi_0$. Here ν labels the irreducible representation, j labels the row of the representation. The choice of the constants v_{α_j} and v_{β_j} depends

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upon the particular method. In this paper the function F_1 is determined so that the resulting $\Psi(1)$ is equal to the exact wavefunction or any given function having the symmetry of A . It is hoped that this analysis will suggest desirable functional forms for F_1 to use in practical problems. Attempts to determine ϕ_1 by optimizing the sum of the first and second order energies were not successful.

There are a great many different theories of exchange perturbations (for reviews, see Refs. (1)-(6)) and most of them would give the exact energy and wavefunction if the treatment were carried to an infinite order. However, in practice, the calculations are sufficiently difficult that the wavefunction is usually truncated after the first order (for examples, see Refs, (7) and (8)). Unfortunately the different methods give different values for the second order energy E_2 and different values for $E(1)$, the expectation value of the Hamiltonian corresponding to the zeroth plus first order wavefunction. In the present paper it is shown that the zeroth plus first order wavefunction obtained by optimizing the basic equation which is used in most exchange perturbation treatments is the exact wavefunction for the perturbed system and $E(1)$ is the exact energy! On the other hand, there is no unique value of E_2 since it can be made arbitrarily large or small. We hope that the equation which we use for determining the optimum first order function will serve as the basis for improving the techniques which can be used to solve practical exchange perturbation problems.

The basic difficulty inherent in exchange perturbation problems is that the symmetry group^{*} corresponding to the perturbed Hamiltonian

*If the Hamiltonian is spin-free, then the energy eigenfunctions (which we call wavefunctions in the present paper) are really the spin-free components of the complete wavefunction. The construction of projection operators to be used in the calculation of the spin-free components of a complete wavefunction is discussed in Refs. (9)-(14).

$H = H_0 + V$ is different from the symmetry group corresponding to the unperturbed Hamiltonian H_0 . Thus, if A is the idempotent projection operator corresponding to a particular irreducible representation (or to a particular row of this irreducible representation) of the symmetry group of the perturbed system, then A commutes with H but not with H_0 . This leads to the relation

$$A H_0 - H_0 A = V A - A V \quad (1)$$

The right-hand-side of Eq. (1) appears to be first order whereas the left-hand-side appears to be zeroth order. Thus, the concept of order is not clearly defined by the "power of V " as in the ordinary Rayleigh-Schrodinger perturbation theory.

Exchange perturbation treatments start with a zeroth order Schrodinger equation

$$(H_0 - E_0)\phi_0 = 0 \quad (2)$$

Here E_0 is taken to be the zeroth order energy, but $\Psi_0 = A \phi_0$, rather than ϕ_0 itself, is generally taken to be the zeroth order wavefunction. We seek approximations to the exact energy E and the exact wavefunction $\Psi = A\Psi$ of the perturbed system. In most exchange perturbation treatments, each order of the perturbed wavefunction has the symmetry of Ψ .

Thus, we seek a first order function ϕ_1 such that the first order wavefunction is $\Psi_1 = A \phi_1$. The wavefunction correct through the first order is then $\Psi(1) = A(\phi_0 + \phi_1)$ and

$$E(1) = \frac{\langle \phi_0 + \phi_1 | A(H_0 + V)A | \phi_0 + \phi_1 \rangle}{\langle \phi_0 + \phi_1 | A | \phi_0 + \phi_1 \rangle} \quad (3)$$

Three observations:

(a) If ϕ_1 is replaced by $\phi_1' = \phi_1 + (1-A)S$, where S is an arbitrary function, then $E(1)$ remains unchanged. This is because ϕ_1 occurs in Eq. (3) only in the form $A\phi_1$.

(b) If V is replaced by either $V' = V + (1-A)T$ or $V'' = V + T(1-A)$, where T is an arbitrary function or operator, then $E(1)$ remains unchanged**. Similarly, H_0 can be replaced by either $H_0 - (1-A)T$ or $H_0 - T(1-A)$.

(c) If ϕ_1 is varied without constraints#, the optimum (or stationary) value of $E(1)$ is obtained when ϕ_1 satisfies the equation $(H - E(1))A(\phi_0 + \phi_1) = 0$. In this case it is clear that $\Psi(1) = \Psi$ and $E(1) = E$. Such a procedure corresponds to the usual variational method.

In the Appendix, Eq. (3) is rewritten in an equivalent form and expanded into terms which correspond to the apparent first, second, ... orders.

It is then shown that the optimum expression for ϕ_1 cannot be obtained by varying ϕ_1 so as to make the sum of the first and second order energies stationary.

** This does not necessarily mean that only the component of V which has the symmetry of A determines the value of $E(1)$. For example, if $A = (1/2)(1-P)$, then it is the $(1-A)$ component of V which enters into Eq. (3) since $AVA\phi$ is equal to the product of $(1-A)V$ times $A\phi$.

Except that it must satisfy the same boundary and continuity conditions as are imposed upon acceptable wavefunctions.

This involves an average between ϕ_1 and ϕ_1' for the reason that ϕ_1 and ϕ_1' are not necessarily orthogonal.

Most Rayleigh-Schrodinger type treatments are based upon rewriting the perturbed Schrodinger equation in the form

$$(H-E)A\Psi = A[(H_0-E_0) + (V-E_1) - E_2 - \dots](\phi_0 + \phi_1 + \dots) = 0 \quad (4)$$

This leads to a first order equation

$$(H_0 - E_0)\phi_1 + (V - E_1)\phi_0 = (1-A)F_1 \quad (5)$$

where F_1 is an arbitrary function[#] and E_1 is the constant which makes Eq. (5) mathematically consistent,

$$E_1 = \frac{\langle \phi_0 | V\phi_0 - (1-A)F_1 \rangle}{\langle \phi_0 | \phi_0 \rangle} \quad (6)$$

The various perturbation schemes differ in their choice[†] of F_1 . In most of the schemes that have been proposed, F_1 is taken^{††} to have the form

$$F_1 = \sum_{\nu, j} \nu A_{\nu jj} (\nu \alpha_j + \nu \beta_j V)\phi_0 \quad (7)$$

Here the ν labels the irreducible representation and j labels the row within that representation. The particular choice of the constants

[†]The various choices of F_1 and the corresponding higher order functions F_2, F_3, \dots which lead to the various perturbation schemes proposed in the literature are discussed in detail in Ref. (15). This paper also presents detailed calculations for H_2 [†] comparing the results for the different theories.

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^{††}Ref. (16) gives the values of $\nu \alpha_j$ and $\nu \beta_j$ corresponding to various proposed treatments. It gives a thorough discussion of the symmetry problems involved in exchange perturbations. Also, it presents accurate calculations for H_2 comparing the results for the different theories.

v_{α_j} and v_{β_j} varies from method to method. Expediency is the only justification for limiting the choice of F_1 in this manner. In the present paper, we seek to optimize F_1 .

Actually, we can show that if $\Psi(1)$ is an arbitrary given function[#] having the symmetry $\Psi(1) = A\Psi(1)$ and E_1 is an arbitrary given value, then it is always possible to find a function F_1 such that Eq. (5) is satisfied by the first order function

$$\phi_1 = -\phi_0 + \Psi(1) + (1-A)G \quad (8)$$

Note that Eq. (8) is consistent with the requirement that $\Psi(1) = A(\phi_0 + \phi_1)$ so that $\Psi(1)$ can be considered to be the perturbed wavefunction truncated after the first order. In Eq. (8), G is any function[#] such that

$$AF_1 = 0 \quad (9)$$

If $AF_1 = 0$, then Eq. (5) (making use of Eq. (8)) gives the identity

$$F_1 = (V-E_1)\phi_0 + (H_0-E_0)[\Psi(1) + (1-A)G] \quad (10)$$

Making use of Eq. (1), the statement that $AF_1 = 0$ can be written in the form

$$A V (1-A)G = A X \quad (11)$$

where

$$X = (V-E_1)\phi_0 + (H_0-E_0)\Psi(1) \quad (12)$$

As will be shown below, for a two particle system (or one containing only gerade and ungerade symmetries), Eq. (11) completely determines

(1-A)G. For a perturbed system with three or more particles (or having more than two symmetry elements), it is always possible to find a function (1-A)G such that Eq. (11) is satisfied, but the solution often is not unique. For such cases, AF_1 and $A\phi_1$ are still uniquely determined by the specification of $\Psi(1)$ and E_1 , but the functions F_1 and ϕ_1 are not uniquely specified.

The optimum function F_1 would be determined by Eqs. (10)-(12) in which $\Psi(1)$ is taken to be the exact perturbed wavefunction Ψ . In this case the $E(1)$ of Eq. (3) becomes the exact energy E .

EXAMPLE: The S_2 Permutation Group

The simplest physical examples of exchange perturbations are the interactions of a hydrogen atom with either another hydrogen atom or else a proton. In either case, the symmetry group of the perturbed system is the S_2 permutation group having the elements 1 and P. This group has two one dimensional irreducible representations, gerade (g) and ungerade (u). The corresponding projection operators are:

$g_A = (1/2)(1+P)$ and $u_A = (1/2)(1-P)$. It is convenient to let the superscript g or u designate the symmetry component of a function, for example: $g_V = g_A V$. For this S_2 group, we must distinguish two cases:

1) The state under consideration has gerade symmetry so that $A \equiv g_A$. Since $V = g_V + u_V$ and since the product $g_V u_G$ is ungerade and $u_V u_G$ is gerade, Eq. (11) has the unique solution,

$$(1-g_A)G = (1/u_V)g_X \quad . \quad (13)$$

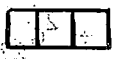


2) The state under consideration has ungerade symmetry so that $A \equiv u_A$. Similarly, since $g_V g_G$ is gerade and $u_V g_G$ is ungerade, Eq. (11) has the unique solution

$$(1-uA)G = (1/uV)^u X \tag{14}$$

If $\Psi(1)$ is a given function and E_1 is a given value then F_1 is uniquely given by Eq. (10) and ϕ_1 is uniquely given by Eq. (8).

EXAMPLE: The S_3 Permutation Group

The exchange of three like particles, as for example in the interaction of H_2 with H , corresponds to the S_3 symmetry group having six symmetry elements. Its three irreducible representations correspond

to the Young diagrams , , and  (which we refer to as 1, 2, and 3 respectively). The projectors for the one dimensional representations 1 and 3 are

$$1A = (1/6)(1 + P_{12} + P_{13} + P_{23} + P_{123} + P_{132}) \tag{15}$$

$$3A = (1/6)(1 - P_{12} - P_{13} - P_{23} + P_{123} + P_{132}) \tag{16}$$

We include the projector $1A$ for the sake of completeness even though a spatial wavefunction which transforms as $1A$ is not Pauli-allowed.

The two dimensional representation 2 has the two projectors

$$2A_{11} = (1/6)(2 + 2P_{12} - P_{13} - P_{23} - P_{123} - P_{132}) \tag{17}$$

$$2A_{22} = (1/6)(2 - 2P_{12} + P_{13} + P_{23} - P_{123} - P_{132}) \tag{18}$$

and the two shift operators*

* Here we are using the convention $A_{ij} = \delta_{ij} \delta_{ij}$. Note that in Goscinski and Lowdin's Ref. (13) notation, the rows and columns are interchanged.

$${}^2A_{12} = (1/12)^{1/2}(P_{13} - P_{23} + P_{123} - P_{132}) \quad (19)$$

$${}^2A_{21} = (1/12)^{1/2}(P_{13} - P_{23} - P_{123} + P_{132}) \quad (20)$$

The projector corresponding to the character of 2A is, of course,

$${}^2A = {}^2A_{11} + {}^2A_{22} = (1/3)(2 - P_{123} - P_{132}) \quad (21)$$

After reducing the representation of VG to its irreducible components (and using the notation ${}^2A_{ij} V = {}^2V_{ij}$), the four symmetry components of Eq. (11) are

$${}^1X = 1/2[{}^2G_{11} {}^2V_{11} + {}^2G_{21} {}^2V_{21} + {}^2G_{22} {}^2V_{22} + {}^2G_{12} {}^2V_{12}] + {}^3G {}^3V \quad (22)$$

$${}^2X_{11} = {}^1G {}^2V_{11} + 1/2[{}^2G_{22} {}^2V_{22} - {}^2G_{12} {}^2V_{12}] + {}^2G_{22} {}^3V + {}^3G {}^2V_{22} \quad (23)$$

$${}^2X_{22} = {}^1G {}^2V_{22} + 1/2[{}^2G_{11} {}^2V_{22} + {}^2G_{21} {}^2V_{12}] + {}^2G_{11} {}^3V + {}^3G {}^2V_{11} \quad (24)$$

$${}^3X = {}^1G {}^3V + 1/2[{}^2G_{11} {}^2V_{22} - {}^2G_{21} {}^2V_{12} + {}^2G_{22} {}^2V_{11} - {}^2G_{12} {}^2V_{21}] \quad (25)$$

In addition, we obtain the equation corresponding to the character projector 2A

$${}^2X = {}^1G {}^2V + {}^3G {}^2V \quad (26)$$

For each of the symmetry cases Eq. (22), or (23) or (24) or (25), provides one condition on the four independent components* of G (1G , ${}^2G_{11}$, ${}^2G_{22}$, and 3G).

* Note that ${}^2G_{21} = {}^2A_{21} {}^2G_{11}$ and ${}^2G_{12} = {}^2A_{12} {}^2G_{22}$ so that ${}^2G_{21}$ and ${}^2G_{12}$ can be determined from a knowledge of ${}^2G_{11}$ and ${}^2G_{22}$ respectively.

Hence G and $(1-A)G$ can be chosen in an infinite number of ways.

On the other hand, if we used the character projector to express the symmetry of the two dimensional representation, we would obtain from Eq. (26) the unique solution for $(1 - {}^2A)G$, corresponding to wavefunctions which have the 2 symmetry,

$$(1 - {}^2A)G = {}^2X / {}^2V \quad (27)$$

Thus, some simplification in the determination of $(1-A)G$ and in the equation (5) for the determination of ϕ_1 may result from the use of the character projector 2A . However, the wavefunction for the perturbed system has the symmetry corresponding to a particular row of the irreducible representation. Thus, $\psi(1) = {}^2A_{11}(k\phi_0 + \phi_1)$ or $\psi(1) = {}^2A_{22}(k\phi_0 + \phi_1)$. As far as the equations for 1X and 3X are concerned, no simplification results from trying to use the 2A projector. For wavefunctions having either the 1 or the 3 symmetry, a particular solution for $(1-A)G$ results from choosing ${}^2G_{11}$ and ${}^2G_{22}$ to be zero (hence ${}^2G_{21} = {}^2G_{12} = 0$). In this case, Eqs. (22) and (25) give

$$(1 - {}^1A)G = {}^1X / {}^3V \quad \text{and} \quad (1 - {}^3A)G = {}^3X / {}^3V \quad (28)$$

We believe that our analysis has shed a bit of light on the structure of the exchange perturbation equations. It remains to be seen how this analysis will be used to develop better functions F_1 which will make the practical solution of exchange perturbation problems easier or more accurate.

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APPENDIX

An Attempt to Determine ϕ_1 by Optimizing $E_1 + E_2$

It is not easy to determine the various orders of perturbation energy from Eq. (3). For example, the apparent zeroth order energy would seem to be

$$E'_0 = \langle \phi_0 | A H_0 A | \phi_0 \rangle / \langle \phi_0 | A | \phi_0 \rangle \quad (A1)$$

instead of E_0 . This difficulty disappears if we rewrite Eq. (3) in the form

$$E(1) = \frac{\langle \phi_0 + A\phi_1 + (1-A)\phi_1 | (A H_0 + H_0 A) + (A V + V A) | \phi_0 + A\phi_1 + (1-A)\phi_1 \rangle}{2 \langle \phi_0 + \phi_1 | A | \phi_0 + \phi_1 \rangle} \quad (A2)$$

Here we are expressing the first order function ϕ_1 as the sum of its two components $A\phi_1$ and $(1-A)\phi_1$, which can be varied separately. In Eq. (3), the zeroth order operator $(A H_0 + H_0 A)$ and the first order operator $(A V + V A)$ are still Hermitian. However, we would have obtained the same conclusions if we had used the non Hermitian zeroth and first order operators $A H_0$ and $A V$ (or equivalently, $H_0 A$ and $V A$). Our conclusion is that we cannot obtain an optimum first order function ϕ_1 by varying the sum of the first and second order energies.

For convenience, let us normalize ϕ_0 so that

$$\langle \phi_0 | A | \phi_0 \rangle = 1$$

Expanding the right hand side of Eq. (A2) and grouping the terms according to their apparent order of perturbation, and letting c.c. denote the conjugate complex we obtain:

$$E_1 = E_1^{\text{HL}} + B_1 \quad (\text{A3})$$

$$E_2 = E_2' + D_2 - \frac{1}{2} B_1 d \quad (\text{A4})$$

Here E_1^{HL} is the usual Heitler-London first order energy

$$E_1^{\text{HL}} = \frac{1}{2} \langle \phi_0 | AV + VA | \phi_0 \rangle \quad (\text{A5})$$

The additional first order energy term is

$$B_1 = \frac{1}{2} [\langle A\phi_1 + (1-A)\phi_0 | (H_0 - E_0)A | \phi_0 \rangle + \text{c.c.}] \quad (\text{A6})$$

The second order energy terms are

$$E_2' = \langle A\phi_1 | H_0 - E_0 | A\phi_1 \rangle \quad (\text{A7})$$

$$+ \frac{1}{2} [\langle (1+A)\phi_0 | V - E_1^{\text{HL}} | A\phi_1 \rangle + \text{c.c.}]$$

$$D_2 = \frac{1}{2} [\langle (1-A)\phi_0 | (H_0 - E_0)A\phi_1 + (V - E_1^{\text{HL}})A\phi_0 \rangle + \text{c.c.}] \quad (\text{A8})$$

and the third term is $-\frac{1}{2} B_1 d$ where

$$d = \langle \phi_0 | A\phi_1 \rangle + \text{c.c.} \quad (\text{A9})$$

Although the function $(1-A)\phi_1$ does not affect $E(1)$, by varying $(1-A)\phi_1$ values of E_1 and E_2 can be made arbitrarily large or small. This follows from the fact that the expressions for E_1 and E_2 are linear in $(1-A)\phi_1$.

We might still expect to obtain a good expression for ϕ_1 by varying $A\phi_1$ (while holding $(1-A)\phi_1$ constant) so as to make the sum of $E_1 + E_2$ stationary. In order for the resulting equation to be mathematically consistent, B_1 must be equal to zero or $E_1 = E_1^{HL}$. The resulting equation for the first order function $\phi_1 = A\phi_1 + (1-A)\phi_1$ (where the $A\phi_1$ has been optimized while $(1-A)\phi_1$ has been held fixed) is then

$$A[(H_0 - E_0)\phi_1 + (V - E_1^{HL})\phi_0] + (H_0 - E_0)A(\phi_1 + (1-d)\phi_0) + (V - E_1^{HL})A\phi_0 = 0 \quad (A10)$$

If now Eq. (A10) is multiplied by $(1-A)$ and we make use of Eq. (1), we obtain an equation of the form

$$(1-A)(H_0 - E_0)AY = 0 \quad (A11)$$

where $Y = \phi_1 - d\phi_0$. Again, making use of Eq. (1), Eq. (A11) can be expressed in the form

$$(AV - VA)AY = 0 \quad (A12)$$

However, the basic premise in perturbation theory is that V does not commute with A , so Eq. (A12) can be true only if $AY = 0$. Thus,

$$A\phi_1 = dA\phi_0 \quad (A13)$$

Multiplying Eq. (A13) by ϕ_0^* , integrating and remembering the definition of d , we see that $d = 0$ and so $A\phi_1 = 0$. Thus, we conclude that Eq. (A10) does not have a (useful) solution. As a result, we cannot obtain an optimum first order function ϕ_1 by making use of Eqs. (A3) and (A4) for the first and second order energies.

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