PERTURBATION THEORY OF INTERMOLECULAR FORCES IN THE SMALL OVERLAP REGION. PART I*

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A new perturbational method for the calculation of the interaction between molecules is presented. The method takes into account the proper symmetry requirements for the zero-order wave function, which can be of the Heitler-London type or any better function. Preliminary calculations of the second order energy correction for the ground and the first excited state of the hydrogen molecule show that this method gives reliable results.

1. Introduction

In the usual perturbational calculations of the interaction energy between atoms or molecules one assumes that the zero-order wave function φ_0 is a simple product of the accurate functions of the individual atoms or molecules (polarization approximation). The φ_0 function satisfies

$$H_0\varphi_0 = E_0\varphi_0\,, \tag{1}$$

where

$$\varphi_0 = \varphi_0^a\varphi_0^b \tag{2}$$

and

$$H_0 = H_0^a + H_0^b. \tag{3}$$

The functions φ_0^a and φ_0^b are the eigenfunctions of atomic (molecular) Hamiltonians H_0^a and H_0^b respectively.

However, the accurate wavefunction of the total system should belong to the irreducible representation, say Γ_i, of the symmetry group of the total Hamiltonian. The simple product function given by Equation (2) does not belong to the Γ_i symmetry mode.

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At very large internuclear distances the polarization approximation gives satisfactory results [1]. At smaller distances the proper symmetry of the zero-order wave function must be assured. The symmetry requirements become important in the region where both interacting molecules overlap significantly. As the overlap criterion one can use the value of the integral:

$$S^2 = \langle \varphi_0^a \varphi_0^b | P_{12} | \varphi_0^a \varphi_0^b \rangle = \iint \gamma_a^*(x, x') \gamma_b(x, x') dx dx', \tag{4}$$

where $\gamma_c(x, x')$ is the first order density matrix for atom c and P_{12} denotes the permutation operator which exchanges the co-ordinates of electron 1 from the molecule a and those of electron 2 belonging to the molecule b. The magnitude S^2 seems to be a reasonable extension of the overlap intergral idea beyond the orbital approximation.

For further analysis one can construct a set of projectors A_i such, that $A_i\Phi$ belongs to the Γ_i symmetry mode for any function Φ from the total Hilbert space $\mathfrak{H}$.

The A_i projectors satisfy the familiar relations

$$A_i A_j = A_i \delta_{ij}, \tag{5}$$

$$A_i^+ = A_i, \tag{6}$$

$$\sum_i A_i = 1, \tag{7}$$

$$HA_i = A_i H, \tag{8}$$

where H is the total Hamiltonian.

The function

$$\psi_0^i = N_0 A_i \varphi_0, \tag{9}$$

where N_0 is a normalization constant, has the proper symmetry. It is easy to see that ψ_0^i is not an eigenfunction of the H_0 operator, hence one cannot apply the standard perturbational procedure. There are several perturbation theories, which try to overcome this difficulty [2]. However, it has been pointed out by Hirschfelder, that none of these methods seem to be quite satisfactory and further research in this field is required [3]. In the present paper a new method is proposed, which is based on the Rayleigh-Schrödinger perturbation theory.

2. *Method*

Using Equations (5), (7) and (8) one can write the following chain of equalities [3]

$$H = H \cdot 1 = H \sum_i A_i = \sum_i HA_i = \sum_i HA_i^2 =$$

$$= \sum_i A_i H A_i = H_1 \oplus H_2 \oplus H_3 \oplus \ldots. \tag{10}$$

The Hamiltonian H is an orthogonal sum of operators H_i, each being H reduced to the related symmetry mode. When one is interested in the Γ_i symmetry mode, it is sufficient

to solve the eigenvalue problem solely for H_i. For this reason, henceforth the subscript i will be omitted.

Let us define the projectors

$$Q = |\psi_0\rangle\langle\psi_0| \tag{11}$$

and

$$S = A - Q. \tag{12}$$

They obviously satisfy the relations

$$Q^2 = Q;\ S^2 = S, \tag{13}$$

$$QS = SQ = 0, \tag{14}$$

$$S^\dagger = S;\ Q^\dagger = Q. \tag{15}$$

One can write

$$AH = QHQ + SHQ + QHS + SHS. \tag{16}$$

Let us define a set of normalized functions φ_k

$$\varphi_k = \varphi^a_{n_k}\varphi^b_{m_k} \qquad k = 1, 2, \ldots, \tag{17}$$

where φ^c_n, for $c = a$ and $c = b$, form the basis of the Hilbert space of the molecule c. Let us also define two other sets of functions χ_k and ψ_k

$$\chi_k = \varphi_k - \frac{A_{0k}}{A_{00}}\varphi_0 \tag{18}$$

and

$$\psi_k = N_k A\chi_k \qquad k = 1, 2, 3, \ldots, \tag{19}$$

where

$$A_{kj} = \langle\varphi_k|A|\varphi_j\rangle, \qquad N_k = \langle\chi_k|A|\chi_k\rangle^{-1/2}. \tag{20}$$

One can easily notice that

$$Q\chi_k = 0, \tag{21}$$

$$S\chi_k = A\chi_k \tag{22}$$

and

$$S\psi_k = \psi_k. \tag{23}$$

The definition (18) assures the orthogonality

$$\langle\psi_k|\psi_0\rangle = 0, \text{ for } k = 1, 2, \ldots. \tag{24}$$

Let us orthonormalize the ψ_k functions for $k = 1, 2, \ldots$ to obtain the orthonormal basis $\{\Psi_k\}$ in the $S\mathfrak{H}$ space

$$\Psi_k = \sum_\mu c_{k\mu}\psi_\mu \tag{25}$$

and

$$\langle \Psi_k | \Psi_l \rangle = \delta_{kl}. \tag{26}$$

Those ψ_k functions which in the course of orthonormalization cause finite linear dependencies should be rejected together with their "primitive" functions χ_k. For each function Ψ_k one can define an unnormalized function

$$\Phi_k = \sum_\mu c_{k\mu} N_\mu \chi_\mu. \tag{27}$$

Thus,

$$\Psi_k = A\Phi_k \qquad k = 1, 2, \ldots \tag{28}$$

Let us construct the operator

$$T = \sum_k |\Phi_k\rangle \langle \Psi_k| \tag{29}$$

which is very similar to that of Byers Brown [5]. The operator T satisfies

$$AT = ST = S, \tag{30}$$

$$TA = TS = T, \tag{31}$$

$$TQ = QT = 0. \tag{32}$$

Using the operator T one can divide the term SHS of Equation (16) into two parts

$$SHS = \tfrac{1}{2}(SH_0T + T^\dagger H_0 S) + \tfrac{1}{2}(SVT + T^\dagger VS), \tag{33}$$

where

$$V = H - H_0. \tag{34}$$

In fact, the Equations (34), (8), (5) and (30) justify the following chain of equalities

$$\tfrac{1}{2}(SH_0T + T^\dagger H_0 S) + \tfrac{1}{2}(SVT + T^\dagger VS) =$$

$$= \tfrac{1}{2}(SHT + T^\dagger HS) = \tfrac{1}{2}(SHAT + T^\dagger AHS) = SHS.$$

Now, one can divide the operator AH:

$$AH = \mathscr{H}_0 + \mathscr{V}, \tag{35}$$

where

$$\mathscr{H}_0 = E_0 Q + \tfrac{1}{2}(SH_0T + T^\dagger H_0 S) \tag{36}$$

and

$$\mathscr{V} = \Delta E Q + SHQ + QHS + \tfrac{1}{2}(SVT + T^\dagger VS) \tag{37}$$

with

$$\Delta E = \langle \psi_0 | H | \psi_0 \rangle - E_0. \tag{38}$$

If φ_0 is a product of the exact molecular wave functions φ_0^a and φ_0^b, the terms SHQ and QHS in Equation (37) become zero when the intermolecular distance R goes to infinity. Indeed, for arbitrary function Φ one has

$$SHQ\Phi = SH|\psi_0\rangle\langle\psi_0|\Phi\rangle = \langle\psi_0|\Phi\rangle N_0 SHA\varphi_0 =$$
$$= \langle\psi_0|\Phi\rangle N_0 SV\varphi_0. \tag{39}$$

The last expression is small because $V\varphi_0 \to 0$ as $R \to \infty$. Exactly the same holds for the QHS term. The third term of Equation (37) vanishes at infinity, since $V\varphi_k$ goes to zero at least as R^{-1}.

Note that from Equations (11) and (32) it follows that

$$\mathscr{H}_0\psi_0 = E_0\psi_0. \tag{40}$$

It can be also easily verified that the operators $\mathscr{H}_0$ and $\mathscr{V}$ are self-adjoint and commute with A. Therefore, in solving the eigenvalue problem for the operator AH it is possible to apply the ordinary Rayleigh-Schrödinger perturbation procedure. Treating $\mathscr{V}$ as a perturbation and introducing the formal parameter λ one can expand the eigenfunction ψ and the eigenvalue E as a power series

$$\psi = \psi_0 + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \ldots \tag{41}$$

$$E = E_0 + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots. \tag{42}$$

It is easy to show from Equations (14) and (32) that

$$E^{(1)} = \langle\psi_0|\mathscr{V}|\psi_0\rangle = \Delta E. \tag{43}$$

The second order energy can be calculated from the formula

$$E^{(2)} = \langle\psi^{(1)}|\mathscr{V}|\psi_0\rangle = N_0\langle\psi^{(1)}|V|\varphi_0\rangle, \tag{44}$$

where N_0 is defined in Equation (9).

In order to obtain the first order correction to the wave function, it was practical to use the well known Hylleraas variational principle [6]. The functional to be minimized takes in our case the form

$$\tilde{E}^{(2)} = \tfrac{1}{2}\langle\tilde{\psi}^{(1)}|H_0 - E_0|T\tilde{\psi}^{(1)}\rangle + \tfrac{1}{2}\langle T\tilde{\psi}^{(1)}|H_0 - E_0|\tilde{\psi}^{(1)}\rangle +$$
$$+ N_0\langle\tilde{\psi}^{(1)}|V|\varphi_0\rangle + N_0\langle\varphi_0|V|\tilde{\psi}^{(1)}\rangle. \tag{45}$$

It was assumed that the trial function $\tilde{\psi}^{(1)}$ satisfies the proper symmetry requirements and is orthogonal to ψ_0 *i.e.* $S\tilde{\psi}^{(1)} = \tilde{\psi}^{(1)}$.

It is convenient to expand $\tilde{\psi}^{(1)}$ in terms of ψ_i functions

$$\tilde{\psi}^{(1)} = \sum_{i=1}^{N} a_i\psi_i. \tag{46}$$

The coefficients a_i can be determined in the usual way from the set of linear algebraical equations.

From the practical point of view any good perturbation procedure should give $E^{(1)}+E^{(2)}$ close to the variational result calculated in the same basis set. The calculation of the third order correction to the energy requires the knowledge of the whole matrix of the total Hamiltonian, which is also sufficient to obtain the energy and the wave function by the variational method. It is also known [7], that the interaction energy resulting from a variational calculation does not necessarily suffer from the loss of accuracy.

In the present method $E^{(1)}+E^{(2)}$ is close to the variational result. The number of time consuming exchange integrals, which are necessary for the calculation of $E^{(2)}$ is proportional to the length N of expansion (46). This number is N times smaller than that appearing in the variational calculations based on the minimization of the total energy functional.

It should be stressed that it is necessary for any good perturbational theory of the exchange forces to be consistent with the polarization approximation at large internuclear distances. This means that in the region of vanishing overlap the second order energy should approach the dispersion energy limit.

In order to prove the proper long-range behaviour of the second order energy given by the present method, it is sufficient to insert into the linear equations resulting from the Equation (45) all overlap and exchange integrals equal to zero. Equations obtained in this way are identical with those arising in the polarization approximation.

Finally, it should be noted that it is not necessary to use as φ_0 the simple product $\varphi_0^a \varphi_0^b$. Instead, one can take any function for which

$$V\varphi_0 \to 0 \text{ as } R \to \infty \text{ and}$$

$$\lim_{R\to\infty} (HA\varphi_0 - E_0 A\varphi_0) = 0. \tag{47}$$

In this case one can follow exactly the same way as in the case of the product function.

3. *Numerical example*

Preliminary calculations by the present method have been carried out for the ground ($X^1\Sigma_g^+$) and the first excited ($b^3\Sigma_u^+$) states of the hydrogen molecule at 5 a.u. $\leqslant R \leqslant$ 10 a.u. The interation energy (E_{int}) has been calculated as

$$E_{\text{int}} = E^{(1)}+E^{(2)}. \tag{48}$$

In Equation (45) the trial function consisting of four terms ψ_l has been used, each term constructed from the Slater type orbitals with all exponents equal to 1. This basis has included all possible functions of the type $2p2p$ and $2p3p$. The interaction energies are given in Table I together with the variational energies, which are the best possible values that can be obtained in the same basis set. From Table II one can see that the good coincidence of the energies is not fortuitous, since the wave function (given as an illustration at $R = 8$ a.u. only) calculated by the present perturbational method is very close to the

TABLE I

Interaction energies of the two hydrogen atoms in $X^1\Sigma_g^+$ and $b^3\Sigma_u^+$ states calculated in a small basis set by the present perturbational method and by the variational one. R in a.u., energies in cm^{-1}

R	$X^1\Sigma_g^+$			$b^3\Sigma_u^+$		
	$E^{(1)}$	$E^{(1)}+E^{(2)}$	Variational	$E^{(1)}$	$E^{(1)}+E^{(2)}$	Variational
5	−554.11	−618.28	−618.48	+421.90	+360.61	+360.57
7	−21.13	−32.73	−32.69	+16.53	+ 5.451	+5.459
8	−3.817	−9.193	−9.179	+3.033	−2.190	−2.181
10	−0.1119	−1.5318	−1.5315	+0.0931	−1.3182	−1.3180

TABLE II

The coefficients at the expansion functions in $\psi^{(1)}$ calculated by the present perturbational method and the best possible coefficients calculated by the variational method for $R = 8$ a.u.

Configuration	$X^1\Sigma_g^+$		$b^3\Sigma_u^+$	
	Perturbational	Variational	Perturbational	Variational
$2p_z2p_z$*	$-1.38_{10}-3$	$-1.36_{10}-3$	$-1.46_{10}-3$	$-1.42_{10}-3$
$2^{-\frac{1}{2}}(2p_x2p_x+2p_y2p_y)$	$-8.03_{10}-4$	$-8.33_{10}-4$	$-9.56_{10}-4$	$-9.72_{10}-4$
$2p_z3p_z$	$-2.97_{10}-3$	$-2.97_{10}-3$	$-2.78_{10}-3$	$-2.80_{10}-3$
$2^{-\frac{1}{2}}(2p_x3p_x+2p_y3p_y)$	$-2.31_{10}-3$	$-2.25_{10}-3$	$-2.09_{10}-3$	$-2.06_{10}-3$

*z is the axis of the molecule.

best one (variational). The above numerical results confirm also the correct long-range behaviour of the second order energy $E^{(2)}$. If the internuclear distance R increases, the agreement between perturbational and variational results becomes better. This is understandable if one notes that in the region of vanishing overlap the second order energy approaches the dispersion energy limit.

For computational reasons the authors were able to carry out calculations in a larger basis set at $R = 8$ a.u. only. If one adds to the previous basis set all possible configurations of the $2p3d$, $3d3d$ and $2p4f$ type (eleven expansion functions), one obtains the interaction energies -11.24 cm^{-1} and -4.01 cm^{-1} for the singlet and the triplet state respectively. The corresponding variational results obtained in the same basis set [8] are -11.14 cm^{-1} and -3.98 cm^{-1}. Thus, the previously observed agreement is confirmed.

These preliminary calculations show that the method is able to give reliable results. Its very well known Rayleigh-Schrödinger framework and simplicity of the computational scheme suggests that it may be also useful in treating more complex systems. Further research on this subject is in progress.

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