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H–H-Interactions in the Region of Small Orbital Overlap

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Calculations have been made on the lowest state of H_2 in the region 4—6 a.u. with a view to elucidating some of the problems arising in the perturbation theory of intermolecular forces in the region of small orbital overlap. The conclusions are that a small basis set of non-orthogonal functions, which in a variation calculation gives reasonably good total energies, can give a poor approximation to the second-order perturbation energies.

Variational calculations using the separate basis functions appropriate to induction, dispersion and charge-transfer energies show that these energies may be reasonably added together to reproduce the variational calculations from the total basis set.

Rechnungen für den Grundzustand von H_2 für Abstände zwischen 4 und 6 a. E. wurden zur Klärung einiger Fragen, die bei Störungsrechnungen für intermolekulare Kräfte auftreten, durchgeführt. Dabei ergab sich, daß eine kleine Basis von nicht orthogonalen Funktionen, die bei Variationsrechnungen durchaus gute Resultate liefern, bei Störungsrechnungen zweiter Ordnung versagen kann. Dagegen zeigen Variationsrechnungen mit getrennten Basisfunktionen für Induktions-, Dispersions- und Charge-transfer-Energien, daß solche Teilbeträge sich addieren lassen und dann die Ergebnisse von entsprechenden Rechnungen mit einem vollständigen Basissatz reproduzieren.

L'état fondamental de H_2 a été étudié dans le domaine de 4.6 u.a., afin d'éclaircir certains problèmes apparaissant dans la théorie par perturbation des forces intermoléculaires dans la région de recouvrement orbital faible. La conclusion signifie qu'une base peu étendue de fonctions non orthogonales, qui donne des énergies totales raisonnables par calcul variationnel, peut donner un mauvais résultat pour l'énergie de perturbation au second-ordre. Des calculs variationnels utilisant les bases respectivement appropriées pour les énergies d'induction, de dispersion, et de transfert de charge, montrent que ces énergies peuvent être raisonnablement ajoutées pour reproduire les calculs variationnels utilisant la base totale.

Introduction

There have been many attempts recently to extend the long range theory of intermolecular forces to the intermediate range, where overlap between the two systems becomes non-negligible [1–7]. Several different perturbation methods have been proposed, but little numerical work has been done either to compare the relative merits of the different theories or to assess the relative importance of the different terms in the perturbation expansions[1].

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[1] The following recent work is relevant to the problem.

1. McQuarrie and Hirschfelder [16] and van der Avoird [17] have applied different perturbation techniques to H_2^+ and in both cases obtained satisfactory results. However, H_2^+ being a one-electron system has rather different features from the usual interatomic or intermolecular interaction.

2. Epstein and Johnson [18] have compared the different perturbation techniques for a model two-spin system in a magnetic field and find considerable differences between them. The model has however little relationship to the problem of intermolecular forces for which the perturbation theories were derived.

3. Certain, Hirschfelder, Kolos and Wolniewicz have papers on H_2 in press in which they compare the different perturbation theories for the range 4—8 a.u. Our calculations are less complete than theirs (in particular we did not have the necessary computor facilities to go into the difficult region beyond 6 a.u.) but in part complementary.

Of special interest in the latter category is the significance of charge-transfer energies in such perturbation expansions. It has frequently been assumed that charge-transfer energies may be added to other contributions to give a meaningful total energy [8]. It is, however, easily shown that inclusion of charge-transfer states in an expansion consisting of locally-excited states leads to an overcomplete set and hence in a perturbation method there is the danger of including certain contributions to the energy twice. It would obviously be useful if at least some guide could be obtained to indicate when and how charge-transfer states might be included, but no rigorous rules are as yet available.

We here report some calculations which we hope will elucidate some of the above problems. The system studied is two hydrogen atoms with parallel spins separated by 4–6 a.u. Both perturbation and variational calculations have been carried out using a basis set of states derived from the $1s$, $2s$ and $2p\sigma$ atomic orbitals of both atoms. For the $2s$ and $2p\sigma$ orbitals we have used (a) hydrogenic functions, which are eigenfunctions of the atomic Hamiltonian and (b) Löwdin-Shull orbitals, which are not [9], but which have the well known desirable property of completeness without inclusion of unbound functions. As the basis set is rather small we do not expect to obtain accurate total energies but we think our results will allow some general conclusion to be reached.

Calculations

The states arising from allowing excitations to $2s$ and $2p\sigma$ on each centre can be classified as follows:

G : the ground state ($1s_a$, $1s_b$)
I : four singly-excited states (e.g. $1s_a\,2s_b$)
D : four doubly-excited states (e.g. $2s_a\,2p_{\sigma b}$)
C : four charge-transfer states (e.g. $1s_a\,2p_{\sigma a}$)
C': two excited charge-transfer states (e.g. $2s_a\,2p_{\sigma a}$).

In the London theory of long-range interactions the states I give rise to induction energies and the states D to dispersion energies. C and C' might be included in a perturbation theory of charge-transfer interactions although C' are not generally considered to have any significant effect on ground-state energies.

In the variational calculations we have solved $(\underline{H}-E\underline{S})\underline{x}=0$ for the lowest eigenvalue using different sets of excited states in order to see if a useful separation of the total energy can be obtained.

The energies are quoted in Table 1 relative to that of the normalized antisymmetrized ground state function $\mathscr{A}\psi_0 = |1s_a\,1s_b|$ so that the values obtained from the variational calculation might be directly compared with second and higher order energies in a perturbation expansion. Two types of variational calculations, A and B, were carried out: in A all states were taken to be antisymmetrized products of atomic orbitals $\mathscr{A}\psi_t$; in B only the ground state was antisymmetrized, the excited states being simple products of atomic orbitals. A further possibility would be to allow all states to be unantisymmetrized, but in this case there is no reason why the lowest energy may not be below that of the true antisymmetrized ground state as it can take on the spatial characteristics of the singlet spin ground state. For example with only one excited state $1s_a\,2p_{\sigma b}$ the lowest energy at 5 a.u. is -1.000350 whereas an accurate function of Kolos

Table 1

States	Hydrogenic A			Hydrogenic B			Löwdin-Shull A			Löwdin-Shull B		
	$R=4$	$R=5$	$R=6$	$R=4$	$R=5$	$R=6$	$R=4$	$R=5$	$R=6$	$R=4$	$R=5$	$R=6$
$I+D+C+C'$	−91.7	−17.1	−4.3	−73.6	−15.6	−3.9	−154.7	−35.5	−10.2	−180.7	−38.5	−10.8
$I+D+C$	−87.5	−15.1	−3.6	−73.2	−15.0	−3.7	−153.6	−34.8	− 9.9	−180.4	−37.3	−10.1
$I+D$	−69.0	−12.8	−3.4	−61.4	−10.9	−2.7	− 81.5	−21.0	− 7.5	− 78.2	−20.1	− 7.3
$I+C$	−81.6	−11.6	−1.6	−53.9	− 9.1	−1.5	−118.3	−19.4	− 3.1	−107.4	−17.5	− 2.8
$D+C$	−45.1	−10.5	−3.3	−56.0	−12.9	−3.5	−150.5	−34.4	− 9.9	−174.2	−36.7	−10.1
I	−52.1	− 6.1	−0.6	−42.8	− 5.2	−0.5	− 11.0	− 0.8	− 0.1	− 9.9	− 0.8	− 0.1
D	−32.9	− 7.5	−2.2	−17.9	− 5.6	−2.2	− 70.7	−19.9	− 7.5	− 68.9	−19.4	− 7.3
C	−40.0	− 7.3	−1.3	−37.2	− 7.0	−1.2	−116.1	−19.1	− 3.1	−101.1	−16.9	− 2.7

Second order energies calculated variationally. R is in atomic units and energies are in units of 10^{-5} a.u. Type A calculations were done using all states antisymmetrized, B with only the ground state antisymmetrized.

Table 2

		Hydrogenic			Löwdin-Shull		
R		4.0	5.0	6.0	4.0	5.0	6.0
$\frac{(I+D+C)}{(I)+(D)+(C)}$	A	.70	.75	.87	.75	.84	.95
	B	.75	.84	.95	1.01	1.00	1.00
$\frac{(I+D)}{(I)+(D)}$	A	.71	.94	1.21	1.00	1.01	.99
	B	1.11	1.01	1.00	.99	1.00	.99
$\frac{(I+C)}{(I)+(C)}$	A	.89	.87	.84	.93	.97	.97
	B	.67	.75	.88	.97	.99	1.00
$\frac{(C+D)}{(C)+(D)}$	A	.62	.71	.94	.81	.88	.93
	B	1.02	1.02	1.03	1.02	1.01	1.01

Additivity relationships for the variational energies. Cases A and B are as in Table 1.

and Wolniewiez [10] has an energy of only −.9986849. It is true that if only the ground state is antisymmetrized there is no method of ensuring that the lowest energy state is spatially antisymmetric but for rather weak interactions this would hardly seem to be a problem.

We also give in Table 3 a *total* second and higher order energy, which we define as the exact energy (assumed to be that of Ref. 10) minus the zero and first order energies.

In Table 2 we make a comparison of the additivity of the different sets of results. For instance $(I+D+C)/[(I)+(D)+(C)]$ is the energy (given in Table 1) calculated from a set of G, I, D and C divided by the sum of the energies calculated from G and I, G and D, and G and C.

The perturbation results are calculated from the formulae in Ref. 4. If the zero order Hamiltonian and wave function are taken to be those of the system at infinite separation then the second-order energies are

$$E^{20} = \sum_{t \neq 0} U_{t0}^2/(E_0 - E_t)$$

and

$$E^{22}=\sum_{t\neq 0} U_{t0}(U'_{t0}-U_{00}S'_{t0}-U_{t0}S'_{00})/(E_0-E_t)\,,$$

the latter being the exchange term. The first-order energy is the energy of the antisymmetrized product relative to the energy at infinite separation, i.e.

$$E^{10}=\frac{U_{00}-U'_{00}}{1-S'_{00}}\,.$$

These formulae apply only for a basis of locally excited states. For the charge transfer states we used the well known formula

$$E^2=\sum_{t\neq 0}(U_{t0}-U_{00}S_{t0})^2/(E_0-E_t)$$

which is formally of exchange type.

Table 3

States	Hydrogenic			Löwdin-Shull		
	$R=4$	$R=5$	$R=6$	$R=4$	$R=5$	$R=6$
I_1	− 10.3	− 1.2	− 0.1	− 10.6	− 0.6	0.0
D_1	− 6.3	− 3.3	− 1.8	− 37.7	− 16.8	− 7.3
I_2	+ 26.9	+ 3.6	+ 0.3	+ 17.5	+ 1.1	+ 0.1
D_2	− 3.8	− 0.8	− 0.1	− 10.0	− 1.4	0.0
C	− 11.2	− 1.5	− 0.2	− 46.9	− 27.6	− 0.9
E^1	+879.0	+192.2	+39.2	+879.0	+192.2	+39.2
E''	−216.8	− 60.7	−20.4	−216.8	− 60.7	−20.4

Energies calculated from perturbation theory. Units are as in Table 1. The subscript 1 indicates the non-exchange terms and 2 the exchange terms. E^1 is the first order energy and $E''=E_{\text{exact}}-E^1-E^0$ is the total second and higher order energies.

Although these formulae apply only when the excited states are eigenfunctions of the H_0 we have used them for the Löwdin-Shull set of orbitals with the modification that E_t is defined as the expectation value of the H_0 for the state t. The results are given in Table 3.

All integrals were computed using the Miller-Brown program [11] and the energies obtained by diagonalization of the matrix $L^{-1}H(L^{-1})^\dagger$ with L defined by $LL^\dagger=S$, using standard routines.

Discussion of Results

We first note from Table 3 that the total second and higher order energies E'' contribute only about 20% to the total interaction energy $(E'+E'')$ at 4 a.u. and 35% at $R=6$ a.u. This result which has been noted before [12] shows that even at fairly large separations the first order energy can not be neglected as it is in the long-range Eisenshitz-London theory.

From the results shown in Tables 1–3 the following points emerge.

1. By comparing the first and second rows of Table 1 it is seen that the states C' are of little importance.

2. If a small basis set is used for this type of calculations and the primary object is the best possible total energy then it is better to use Löwdin-Shull orbitals than hydrogenic ones. This is to be expected.

3. In the long range limit the order of importance is known to be dispersion $\gg$ induction $>$ charge transfer. Donath and Pitzer [12], who have made calculations for $R = 6$ and above, have noted that even at quite long internuclear distances electron correlation effects (introduced by mixing in charge transfer terms) play a significant role. Our results quite clearly confirm that the long-range order does not hold at the relatively short distances we are studying. At some distance below the van der Waal's radius (which for this state is ≈ 8 a.u.) the induction and charge-transfer energies become larger than the dispersion energy for our small basis set. We do not of course know if this is true for the complete set.

4. As mentioned earlier one of the main problems in the theory of intermolecular forces is the influence of charge transfer states. If a perturbation theory of exchange forces is based on the complete set of locally excited states then a rigorous separation of the total energy can be obtained. If charge transfer states are added to the set it becomes overcomplete and moreover these states are not eigenfunctions of the unperturbed Hamiltonian. In whatever way one chooses to calculate charge transfer energies they will not be expected to be additive to the dispersion or induction energies. This non-additivity is shown for the variational calculations in Table 2. It is seen however that the charge transfer energy is neither more nor less additive than the inductive and dispersion energies at these distances. In general additivity is improved as R increases, but clearly in certain cases the expected convergence to unity occurs at longer distances than we have studied. One further general point is that additivity is better in type B calculations than in A, suggesting that deviations from additivity are due mainly to the interaction between different excited states rather than between the excited state and the ground state.

The results show that if one is using a small basis set charge transfer states make an important contribution to the total energy yet there will be no single perturbation formula which allows one to add a charge-transfer energy to inductive and dispersion energies.

5. We turn now to the perturbation results shown in Table 3. The most obvious characteristics are (a) the overall smallness compared to the variational results and to the exact higher order energy and (b) the relatively large size of some of the exchange contributions.

The overall smallness compared with the exact higher order energies is expected and is fully consistent with known results. As early as 1930 Eisenshitz and London [13] calculated that 40% of the dispersion energy in H_2 comes from the continuum and it is generally accepted that the series for E^{20} is only very slowly convergent for an expansion in terms of eigenfunctions. The results are rather better for the Löwdin-Shull expansion set. The second order exchange terms (E^{22}) have received little attention, although Alexander and Salem [14] have calculated "generalized" exchange and dispersion energies for the interaction of two hydrogen atoms and their results are not inconsistent with ours. Little is known about the behaviour of the second order exchange terms. Although Musher and Amos [15] claim that the main contribution to these energies comes from the continuum; this is not supported by our results. The large size of these exchange terms is not unexpected at these distances as the overlap between the 1*s* orbital of one atom and the 2*s* and 2*p* orbitals of the other are quite large (see Table 4).

Table 4

	Hydrogenic			Löwdin-Shull		
	$R=4$	$R=5$	$R=6$	$R=4$	$R=5$	$R=6$
$S_{1s_a 1s_b}$	.1893	.0966	.0471	.1893	.0966	.0471
$S_{1s_a 2s_b}$	−.2814	−.2702	−.2352	−.2820	−.1945	−.1202
$S_{1s_a 2p\sigma_b}$	.4776	.4157	.3377	.3785	.2414	.1413

Overlap integrals for certain of the orbitals used in this paper.

It is perhaps surprising that although the small basis set is clearly insufficient to give reasonable values of the perturbation energies nevertheless it gives a fairly good result when used in the variation calculation. The reason is that when the basis is far from complete and non-orthogonal, the omission of certain terms from the basis is compensated by an increase in the effect of other states. However, in perturbation theory taken to second order each excited state contributes independently to the total energy and the omission of certain states from the set cannot be compensated for.

Conclusion

The conclusions from this work are that for distances just short of the van der Waals minimum perturbation calculations using a small basis set of eigenfunctions of the separated system will not give satisfactory higher order energies. We have not been able in this study to say if this conclusion extends to distances larger than the van der Waals radii but we suspect that it does. A small basis of eigenfunction may be useful for a variational calculation, but, better results are likely to be obtained using a carefully chosen basis which are not eigenfunctions. This approach is now being studied.

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