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Ab-initio valence bond calculations on the He–He potential curve using small bases†

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In studying methods for the ab-initio calculation of Van der Waals interactions which can be extended to larger molecules, we have tested the Valence Bond scheme on the He₂ system. This method looks promising, as it appears to yield in one consistent formalism both the attractive dipole–dipole terms and the repulsive exchange terms with reasonable accuracy, using only a simple orbital basis and a very small number of VB structures.

1. Introduction

The interaction between two ¹S ground-state He atoms has been investigated by many people with methods of varying degrees of accuracy and sophistication. The older approaches (e.g. reference [1]) use perturbation formalisms which account for the long-range Van der Waals attraction, and superpose empirical repulsive potentials in an ad hoc manner, in order to give good fits to the depth and position of the Van der Waals minimum. Later workers [2–4] concentrated on the exchange interaction, mainly using an MO scheme. These investigators were not able to obtain minima in the potential curves, so one started to realize that the computation within a uniform model of a complete interaction curve for He₂ poses a real problem. Even the 64-term Configuration Interaction wave function of Phillipson [5] did not predict the correct depth of the Van der Waals minimum. One still had to obtain the repulsive and attractive contributions to the energy by separate calculations [6]. This situation remained unaltered all through the sixties [7–10], which led to the now common conviction that a single configuration potential curve for two closed-shell atoms must be entirely repulsive [11].

In 1970 two independent simultaneous publications [12, 13] presented high quality potential curves, each calculated by a single consistent computational technique. Although these results prove beyond doubt that the Van der Waals potential well can be computed with an accuracy comparable to that of experiment, it will be difficult to apply these methods to larger systems.

The purpose of this communication is to point out that reasonable results can be obtained by very simple calculations; that is, simple with regard to the size of the basis sets and the computer time spent on the whole curve. Only if one is

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able to predict with minimal effort the Van der Waals energy of a small system like He–He will it be possible to hope for positive results in computations on larger systems.

2. Method

The Valence Bond (VB) method is similar to a perturbation treatment in the sense that it is based on the states of the unperturbed atoms. In VB theory, one solves a secular problem in which an element of the hamiltonian matrix has the general form

$$H_{ij} = \langle \mathcal{A} P_s \Psi^A \Psi^B | H | \mathcal{A} P_s \Psi^A \Psi^B \rangle.$$  \hspace{1cm} (1)

Here $\mathcal{A}$ is the antisymmetrizer for the total system, $P_s$ a spin-adapting projection operator and $\Psi^A, \Psi^B$ are unperturbed states of the atoms A and B respectively.

The two main problems in the computation of $H_{ij}$ are the effect of $P_s$ and the non-orthogonality between the orbitals on the atoms A and B. The matrix elements (1) are constructed by Reeves’ algorithm [14] which is based on a Young projector [15].

This algorithm expects orthonormal spatial orbitals, and so we orthonormalize a chosen set of atomic orbitals by means of a matrix $t$. Then the full $H$-matrix $H$ with elements defined by (1) is constructed on the basis of all states (with a certain spin multiplicity) which arise from the orthonormalized AO set. The effect of the orbital transformation $t^{-1}$ on the $A$-electron wave functions is given by an Nth-order tensor representation [16] $T(t^{-1})$ which undoes the effect of $t$ after performance of the transformations

$$O = H'C' - S'CE = T'(t^{-1})HT(t^{-1})T(t)C - T'(t^{-1})ST(t^{-1})T(t)CE.$$  \hspace{1cm} (2)

Specific VB structures can be selected by considering only certain columns of $T(t^{-1})$ and so the dimension of the primed secular equation, which is on the basis of the original non-orthogonal AO’s, is generally smaller than the dimension of the $H$-matrix defined by (1). Solution of the transformed equation in the usual manner gives the desired VB states and energies.

In this procedure, which we intend to elaborate in a future publication, one avoids tedious derivations of matrix-elements on basis of non-orthogonal orbitals.§

The exact form chosen for the matrix $t$ is unimportant if the effect of the orthonormalization is annihilated according to equation (2). However, for large problems this is not feasible and in that case the choice of a good orthonormalization procedure [17] becomes important. We have promising experiences with the following three-step process:

(i) Löwdin-orthonormalize the orbitals occupied in the free atoms.
(ii) Perform a Gram–Schmidt orthonormalization of the remaining orbitals onto the occupied ones.
(iii) Löwdin-orthonormalize the orbitals obtained in step (ii) among each other.

§ We thank the referee for drawing our attention to two papers [25, 26] which treat the non-orthogonality problem in a similar way. In these references the secular matrices are defined on the basis of Slater determinants instead of Young projected functions. Although the use of Slater determinants facilitates the construction of $T(t^{-1})$, it requires a much larger dimension of the secular problem, since one does not work with eigenfunctions of $S^2$. 


Programmes based on the outlined ideas have been written for an IBM 370/158 computer, taking as integral input the output from the IBMOL-5 programme [18].

3. Results

On each He atom the four orbitals: 1s, 2p_x, 2p_y, 2p_z are placed. The 1s orbitals (SCF orbitals from Huzinaga [19]) are represented by a contracted set of six primitive gaussians. Also six primitives are contracted to represent a single-ξ Slater-type p orbital. The exponent ξ_p of this STO can be optimized in four different ways, see table 1.

<table>
<thead>
<tr>
<th>Energy minimized</th>
<th>ξ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlated atomic 1S energy</td>
<td>2.45</td>
</tr>
<tr>
<td>Excited state SCF 3P energy</td>
<td>0.58</td>
</tr>
<tr>
<td>Excited state SCF 3P energy</td>
<td>0.47</td>
</tr>
<tr>
<td>Van der Waals energy He–He at R = 5.6 bohr</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 1. Optimized STO exponents ξ_p of the 2p orbital.

The value ξ_p = 1.3 compares well with the value ξ_p = 1.378 found from an analytic optimization of the Van der Waals attraction [20]; the other values in table 1 agree with those given in reference [12]. In all subsequent calculations the value of ξ_p is held fixed on 1.3. The first calculations are based on the four σ-type AO's only. Although the usual perturbation approach [11] starts from purely co-valent states, yet we started with a set of 'full' VB calculations. Since four AO's give rise to at most 20 singlet structures, full VB implies a 20-dimensional secular problem. The results are shown in figure 1.

Compared to the experimental values [21]: E_m/k = 11.0 K and R_m = 5.6 bohr† the minimum is much too deep. Inspection of the wave function Ψ at the minimum, while retaining only the dominant terms

\[ Ψ = 0.999 \left[ s_A^2, s_B^2 \right] - 0.034 \left[ \left[ s_A^2, p_B^2 \right] + \left[ p_A^2, s_B^2 \right] \right] \]
\[ - 0.005 \left[ \left[ s_A^2, p_A, p_B \right] + \left[ p_A, p_B, s_B^2 \right] \right] + 0.004 \left[ s_A, p_A, s_B, p_B \right] \]

shows that the leading structure represents the Hartree-Fock uncorrelated ground state in the separated atom limit. The last term in Ψ is the one predicted by perturbation theory to be responsible for the induced dipole-induced dipole part of the dispersion energy [11]. The second structure \( s_A^2, p_B^2 \) is known to contribute considerably to the intra-atomic correlation energy of atom B, and \( p_A^2, s_B^2 \) does the same for atom A. But we expect a more or less constant shift of the potential curve from these latter terms, as the intra-atomic correlation energy does not depend heavily on \( R \) [22]. This is confirmed by the coefficients of the first three structures which are practically independent of \( R \) up to the separated atom limit.

Unexpected is the presence of the excited CT (charge transfer) structures \( s_A^2, p_A, p_B \) and \( p_A, p_B, s_B^2 \) while the CT states \( s_A^2, p_A, s_B \) and \( s_A, p_A, s_B^2 \) are

† \( k = 1.38054 \times 10^{-23} \text{ J/K} \) (Boltzmann's constant). 1 bohr = 5.29167 \times 10^{-11} \text{ m}. 

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absent. After a moment of thought the relative importance of these terms can be explained as follows. Making the formal expansion of \( p_A(r_A) \) in a set of atomic functions centred on B:

\[
P_A(r_A) = \sum_{n,l} C_{nA}(R) f_{nA}(r_B)
\]

we write

\[
[s_A^2, p_A, s_B] = \sum_{n,l} C_{nA}(R)[s_A^2, f_{nA}(r_B), s_B(r_B)].
\]

The right-hand side of this equation is an expansion in singly excited states on atom B, which, \( s_B(r_B) \) being an SCF orbital, does not contribute to the ground-state via intra-atomic terms in the Hamiltonian operator. (Even in the case of non-orthogonal orbitals [27] it can be proved easily, by invoking Brillouin’s theorem, that the admixture of singly excited states leaves the ground state of atom B a pure \([s_B^2] \) state.) This explains the unimportance of CT terms without simultaneous excitation.

In the same way the excited CT structure becomes

\[
[s_A^2, p_A, p_B] = \sum_{n,l} C_{nA}(R)[s_A^2, f_{nA}(r_B), p_B(r_B)],
\]
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from which we deduce immediately that this structure yields a contribution to the intra-atomic correlation energy of atom B. Because of the \( R \)-dependent expansion coefficient \( C_{n,l} (R) \) this contribution is distance dependent. To get a better grasp of this distance-dependent improvement of the intra-atomic correlation energy we performed VB calculations on the free He atom A, with a basis of structures on the ‘empty’ (no electrons, no nucleus) centre B approaching A. The results are plotted in figure 2. The influence of the basis on B is seen to grow drastically with decreasing distance. It is important to note that the He atom is physically unperturbed, and that this artificial energy lowering is a mathematical effect due to the enlargement of the structure basis. Around 5.5

Figure 2. Distance dependency of the energy of the He atom A in the structure basis of A + B, multiplied by 2. Only the structures with non-negligible contribution are indicated.

bohr this energy lowering is of the same order of magnitude as the physical interaction between two He atoms, but together with the physical interaction this energy does not fully add up to the well depth of the full VB calculation. So we must conclude that the effect of the basis set enlargement is not an additive one and, therefore, to eliminate this phenomenon we omit all structures that contribute to the intra-atomic correlation, in accordance with the purpose of this investigation†. In figure 3 three computed potential curves are exhibited. The

† After completion of this work a paper on the He–He interaction [28] appeared which also considers in detail the effect of basis enlargement. The authors use a larger atomic orbital and configuration basis. They perform a large Configuration Interaction calculation and correct for the distance-dependent basis-set effect by subtracting the result of an atomic calculation with a vacant basis on the other centre, thus assuming additivity.
upper two are calculated with $\sigma$-type AO's, taking into account the two co-valent structures \([s_A^2, s_B^2] \) and \([s_A, p_A, s_B, p_B]\) only. The lower of these two is obtained from pure, non-orthogonal AO's, and the higher one from AO's that are orthogonalized by the three-step process described in the previous section. Notice that because of the careful orthogonalization the curves almost coincide.

We have tried several other ways of orthonormalization, for instance SCF followed by localization, but they all give results that are definitely inferior to the ones shown.

![Figure 3. Van der Waals energy calculated by VB on the basis of four $\sigma$ orbitals (two structures) or eight $\sigma + \pi$ orbitals (four structures).](image)

The lowest of the three curves in figure 3 has been computed by inclusion of two $\pi$ AO's on each atom and the four structures:

\[
[s_A^2, s_B^2], [s_A, p_{xA}, s_B, p_{xB}], [s_A, p_{yA}, s_B, p_{yB}], [s_A, p_{xA}, s_B, p_{xB}].
\]

Here the AO's are orthogonalized, again following the described three-step scheme.

All doubly-excited configurations give rise to two linearly independent singlet VB structures. One of these structures corresponds to the coupling of
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two excited singlet He atoms, the other one to the coupling of two excited triplet atoms [15]. It appears that the contributions of the latter structures to the interaction energy are negligible.

4. Discussion

In figure 3 is shown how a very simple calculation based on two σ-type AO's per atom and only two VB structures is capable of giving already an important part of the experimental Van der Waals energy (upper two curves). One cannot expect much more, of course, since in effect only the σ-dependent part of the dipole–dipole interaction [11] is taken into account.

Including the π contributions to the dispersion energy by adding just two more structures it can be concluded that a very simple computation suffices to give a major part of the Van der Waals energy. Here the theoretical limit is the total induced dipole-induced dipole \( R^{-6} \) contribution to the dispersion energy. Kestner [11] estimated this to give a minimum of 5.68 K, but this agrees neither with the results of Schaefer et al. [12, 23], nor with ours.

In table 2 our results are compared with those of Schaefer et al.; the agreement, especially in the outer region, is striking, since these authors based their \( \sigma + \pi \) calculations on five s and pσ orbitals and four pπ orbitals per atom, yielding 72 σ configurations and 16 π configurations.

| \( R \) bohr | SCF \( \langle s_A^2 s_B^2 | H | s_A^2 s_B^2 \rangle \) | \( \sigma(\sigma + \pi) \) | \( \pi(\sigma + \pi) \) |
|-------------|-----------------|-----------------|-----------------|
| 5·2         | 24·45           | 23·43           | +7·7            | +8·08           | −0·6            | +0·57           |
| 5·4         | 15·03           | 14·11           | +1·7            | +1·64           | −5·0            |
| 5·6         | 9·24            | 8·46            | −1·6            | −1·71           | −7·0            | −6·63           |
| 5·8         | 5·66            | 5·05            | −3·08           | −3·25           | −7·46           | −7·26           |
| 6·0         | 3·45            | 3·00            | −3·64           | −3·82           | −7·17           | −7·14           |
| 6·2         | 1·77            | −3·85           | −5·90           |
| 6·4         | 1·04            | −6·60           | −5·56           |
| 6·5         | 1·00            | −3·38           | −4·48           |
| 6·6         | 0·63            | −3·25           | −3·90           |
| 6·8         | 0·32            | −2·87           | −1·83           |
| 7·0         | 0·287           | −2·51           | −0·92           |
| 8·0         | 0·023           | −1·23           | −0·28           |
| 9·0         | 0·002           | −1·17           | −0·49           |
| 10·0        | 0·000           | −0·57           | −0·85           |
| 12·0        | 0·000           | −0·09           | −1·83           |
| 14·0        | 0·000           | −0·63           | −0·92           |

Table 2. Interaction energies in units of degrees Kelvin. The SCF energy for two isolated He atoms is −5·722 232 8 hartree.

Concluding, it can be stated that the VB method performs very well for weakly interacting systems such as two He atoms. It constitutes a single consistent model capable of giving a good prediction of the entire Van der Waals well.

Of course, in this work the intra-atomic correlation correction is neglected by using a Hartree–Fock atom as the reference system. At the Van der Waals minimum, however, this correction differs only 1·23 K from the correlation energy.
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in the free atoms [23]. Although this difference increases for shorter interatomic distances [24], it remains rather small relative to the repulsion energy. Moreover, the VB scheme can only be expected to perform well if the atoms do not deviate too much from their electronic structure at infinite distance. If one is interested in the repulsive region at smaller distances, an approach based on the Hartree–Fock molecule as the reference system seems more appropriate, unless one is prepared to include substantially larger numbers of VB structures than we did in this paper.

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