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SIMPLIFIED METHODS FOR THE AB-INITIO CALCULATION OF VAN DER WAALS INTERACTIONS INCLUDING EXCHANGE*

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It is demonstrated on the example of H_{2} that the van der Waals energy can be calculated quite accurately by the multi-structure valence-bond method using a relatively simple "effective excited state" model. A simplified procedure for optimization of the excited state orbitals, based on work by Murrell et al., is described. The importance of exchange and charge penetration effects, particularly on the dispersion forces, is quantitatively studied.

1. Introduction

Traditionally van der Waals interactions are calculated by the London theory based on the second order perturbation expression:

\[ \Delta E_L^{(2)} = \sum_{k,k'} \frac{|\langle \phi_0^A \phi_0^B | V^{AB} | \phi_k^A \phi_k^B \rangle|^2}{E_0^A - E_k^A + E_0^B - E_k^B}, \]  

where \( \phi_k^A \) and \( \phi_k^B \) represent the unperturbed wavefunctions and energies of the separate molecules A, B and \( V^{AB} \) is the intermolecular interaction operator. Since it is assumed in this theory that the charge distributions of the monomers A and B are non-overlapping, formula (1) yields only attractive long-range forces. Exchange repulsion has to be calculated separately and added to the long-range interactions in order to obtain a van der Waals minimum. By this procedure the London theory is extended to intermolecular distances around the van der Waals minimum for which it is not valid because of penetration and exchange effects.

The last few years have shown some calculations on small systems such as He_{2} which yielded a complete description of the van der Waals well by one consistent method [1–3]. The techniques which were used, a Hartree–Fock calculation on the dimer followed by rather extensive configuration interaction in one case [1,2], a multiconfiguration SCF calculation in another [3], are so complicated, however, that the application of these techniques to larger systems seems difficult. Recently, Wormer and van der Avoird [4,5] have proposed a multistructure valence-bond (VB) method on the basis of monomer orbitals that is related to the London theory, but takes exchange into account by using correctly antisymmetrized and spin-projected VB structures. Electrostatic and exchange effects between the unpolarized molecules are calculated from the expectation value of the total hamiltonian over the ground state VB structure \( Y \phi_0^A \phi_0^B \), induction and dispersion interactions as well as exchange-polarization effects are obtained by the admixture of excited VB structures \( Y \phi_k^A \phi_k^B \). The Young operator \( Y \) acts on the spin-free wavefunctions in order to impose the permutation symmetry required by the Pauli principle for the given spin eigenvalue [6]. The unperturbed states \( \phi_k^A \) and \( \phi_k^B \), which are approximated by single-configuration wavefunctions, can be obtained from Hartree–Fock (HF) calculations on the separate molecules. If the method is to be applicable to larger systems, however, the number of excited VB structures should be as small as possible and the virtual HF orbitals of the ground
state or even HF orbitals from excited state calculations are probably not the best to achieve rapid convergence of the VB expansion.

We show in this paper on the example of He$_2$ that a quite accurate van der Waals minimum can be calculated with a restricted number of VB structures if the excited state orbitals are optimized especially for this purpose. This optimization can be performed by minimizing the VB energy of the dimer according to a direct search method. A less time consuming method is suggested, though, by the correspondence between our VB model and the London theory: optimize the London interaction energy ($\vec{1}$) after expansion of the operator $F_{AB}$ in a multipole series, so that only monomer transition moments and energy levels need to be evaluated. The optimum excited state orbitals obtained by the latter procedure can then be substituted into a restricted number of VB structures, which are selected by looking at the leading terms in the expanded London formula. In the next two sections we compare these two methods of optimization.

2. Optimization of excited state orbitals in the London multipole formula

Consider two helium atoms A and B. When the multipole expansion of $V^{AB}$ is substituted into (1) the first, dipole—dipole term yields an infinite summation over all singly excited $^1P$ states on A and B. Describing the unperturbed ground state wavefunction by the product $|l_sA \rangle |l_sB \rangle$, the excited states in this summation can be written as: $|l_sA // p_A z \rangle |1 s_B // p_B \rangle$. The configuration symbol denotes singlet wavefunctions, the subscript $m = 1, 0, -1$ runs over the three different (real) angular $p$-functions and the indices $n$ and $n'$ run over the complete set of $p$-orbitals including the continuum. Analogously, the dipole—quadrupole term in $V^{AB}$ gives rise to a sum over $|l_sA // d_A \rangle |l_sn'dfu \rangle$ with $m = 2, 1, 0, -1, -2$. Now it has been found by Murrell et al. [7,8] and by Kockel and Wirsam [9] that the infinite summations over $p_A$ and $p_B$ can be effectively replaced by a single term with a 2p function on A and B. By optimizing the exponent of this 2p orbital in order to maximize the
dipole—dipole contribution to the London energy. Murrell et al. obtained a very accurate estimate of this contribution and the corresponding $C_6$ coefficient in the $R^{-1}$ expansion.

We show the same for the dipole—quadrupole and the quadrupole—quadrupole dispersion energy by calculating the optimized 3d orbital exponent and the resulting $C_8$ and $C_{10}$ coefficients. The effective excited 2p and 3d orbitals are represented by a single-zeta Slater type orbital (STO), the ground state 1s orbital either by a single-zeta STO ($\xi = 27/16 = 1.6875$) or by a double-zeta STO as given by Clementi [10] ($\xi_1 = 1.44608$, $c_1 = 0.83415$, $\xi_2 = 2.86222$, $c_2 = 0.19060$). The monomer transition moments occurring in formula (1) after substituting the multipole expansion of $V^{AB}$ and the energy levels in the denominator of this formula are easily expressed in the parameters to be varied: the 2p and 3d orbital exponents. The energy levels were calculated as expectation values of the exact atomic hamiltonian, since this was shown in ref. [8] to yield better results than the summation of Hartree or Hartree–Fock one-electron energies. The 2p and 3d orbital exponents which lead to a maximum dispersion energy and the resulting $C_6$, $C_8$, $C_{10}$ values are given in table 1.

Also exhibited in this table are $C_6$, $C_8$, $C_{10}$ calculated by the Unsold approximation [11]. For the Unsold average excitation energies in the denominator we have substituted the energies of excitation to the "effective" $1^1P$ and $1^3D$ states ($\Delta E_{1s\rightarrow 2p}$ and $\Delta E_{1s\rightarrow 3d}$ from table 1); in the numerator we have used the closure relation and evaluated the occurring moment expectation values over the ground state wavefunction.

The same idea of using an "effective" [1s 2p] and [1s 3d] state with optimized orbital exponents was adopted by Teixeira-Dias and Varandas [12] for approximating the dynamic dipole and quadrupole polarizabilities $\alpha^{(1)}$ and $\alpha^{(2)}$ of the He atom. We have calculated the static polarizabilities in a rather analogous way (using expectation values of the exact atomic hamiltonian for the unperturbed energy levels, whereas Teixeira-Dias and Varandas used the Hartree one-electron energies) in order to see whether the optimized dispersion energy exponents would also lead to accurate static polarizabilities and vice versa. The results are also given in table 1. Teixeira-Dias and Varandas have also calculated $C_6$, $C_8$ and $C_{10}$ by using an integral formula over frequency-dependent polarizabilities computed from the "effective excited state" model. Note that this procedure is much more complicated, however, than the direct calculation of $C_6$, $C_8$ and $C_{10}$ by the "effective excited state" model, because the latter calculation only requires quantities which were already computed in the evaluation of the polarizabilities.

Some conclusions can already be drawn from table 1. The 2p and 3d exponents obtained from a maximization of the London energy are somewhat different from those which maximize the static polarizabilities. Since these quantities do not depend very sensitively on the exponents, at least in the neighborhood of the optimum, still very reasonable $C_6$, $C_8$, $C_{10}$ values and polarizabilities $\alpha^{(1)}$, $\alpha^{(2)}$ can be obtained from one calculation. On the other hand, all these quantities depend rather strongly on the quality of the 1s orbital. The latter conclusion was also reached by Murrell et al. [7,8] but they found that the increase from a double-zeta to a five-exponent expansion yielded no further improvement.

The fact that the calculations by the Unsold approximation, which are even simpler than the "effective excited state" calculations, also yield good results seems very promising. Apparently, the use of the closure relation in the numerator, instead of calculating the transition moment to a single effective excited state, makes not much difference. One must realize, though, that the tabulated values for the Unsold results were obtained by substituting the excitation energies calculated from the "effective excited state" model, which cannot be computed directly. It is striking that these "effective excitation energies" are even larger than the first ionization energy of the He atom (0.904 au [16]). If the experimental or theoretical energies of excitation to the "physical" singly excited states or the first ionization energy are used in the Unsold expression, the calculated $C_6$, $C_8$, $C_{10}$ values and polarizabilities are much too high (e.g., $C_6 = 2.071$, $C_8 = 20.309$, $C_{10} = 92.93$ for a double-zeta 1s orbital, using the ionization energy).

3. Optimization of excited state orbitals in the valence-bond method

We have repeated the optimization of the 2p and
Table 2

Optimized “second-order” energy contributions from VB and London methods at \( R = 5.65 \) bohr. All values in \( 10^{-5} \) atomic units. Inspection of the VB-results shows different non-additivity effects (dip−dip + dip−quad + quad−quad, \( \sigma + \pi + \delta \))

<table>
<thead>
<tr>
<th>VB-method</th>
<th>( \Delta E^{(2)}_{VB} )</th>
<th>( \Delta \tilde{E}^{(2)}_L )</th>
<th>( \sigma ) dip−dip</th>
<th>( \pi ) dip−dip</th>
<th>( \sigma ) dip−quad</th>
<th>( \pi ) dip−quad</th>
<th>( \delta ) quad−quad</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 ( [\text{ls}^A 2p^A_\sigma \text{ls}^B 2p^B_\sigma] )</td>
<td>-2.99</td>
<td>-3.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3,4 ( [\text{ls}^A 2p^A_\pi \text{ls}^B 2p^B_\pi] )</td>
<td>-1.55</td>
<td>-1.58</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \sigma ) and ( \pi ) structures (2,3,4)</td>
<td>-4.54</td>
<td>-4.74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5 ( [\text{ls}^A 2p^A_\sigma \text{ls}^B 3d^B_\sigma] )</td>
<td>-0.67</td>
<td>-0.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6 ( [\text{ls}^A 3d^A_\sigma \text{ls}^B 2p^B_\sigma] )</td>
<td>-0.07</td>
<td>-0.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7,8 ( [\text{ls}^A 2p^A_\pi \text{ls}^B 3d^B_\pi] )</td>
<td>-0.06</td>
<td>-0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9,10 ( [\text{ls}^A 3d^A_\sigma \text{ls}^B 2p^B_\sigma] )</td>
<td>-0.01</td>
<td>-0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \sigma ) and ( \pi ) structures (5,6,7,8,9,10)</td>
<td>-1.14</td>
<td>-1.34</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11 ( [\text{ls}^A 3d^A_\sigma \text{ls}^B 3d^B_\sigma] )</td>
<td>-0.13</td>
<td>-0.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12,13 ( [\text{ls}^A 3d^A_\pi \text{ls}^B 3d^B_\pi] )</td>
<td>-3.68</td>
<td>-4.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14,15 ( [\text{ls}^A 3d^A_\delta \text{ls}^B 3d^B_\delta] )</td>
<td>-2.08</td>
<td>-2.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \sigma ), ( \pi ) and ( \delta ) structures (11,12,13,14,15)</td>
<td>-0.01</td>
<td>-0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>all ( \sigma ) structures (2,5,6,11)</td>
<td>-3.68</td>
<td>-4.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>all ( \pi ) structures (3,4,7,8,9,10,12,13)</td>
<td>-2.08</td>
<td>-2.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>all ( \delta ) structures (14,15)</td>
<td>-0.01</td>
<td>-0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>all structures</td>
<td>-5.74</td>
<td>-6.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3d orbital exponents in a valence-bond calculation where we solved a secular problem over the following 15 singlet VB structures:

\[
[\text{ls}^A 2s^A_1 \text{ls}^B 2s^B_1], [\text{ls}^A 2p^A_2 \text{ls}^B 2p^B_2], [\text{ls}^A 2p^A_m \text{ls}^B 2p^B_m], m = 1,0,-1 ;
\]

\[
[\text{ls}^A 2p^A_2 \text{ls}^B 3d^B_1], [\text{ls}^A 3d^A_m \text{ls}^B 2p^B_m], m = 1,0,-1 ;
\]

\[
[\text{ls}^A 3d^A_1 \text{ls}^B 3d^B_1], m = 2,1,0,-1,-2 .
\]

The wavefunctions corresponding to these structures are correctly antisymmetrized and spin-projected in order to include exchange effects. Actually, the 14 excited configurations each correspond with two VB structures, one obtained by coupling two atomic singlet states, the other by coupling two triplets. The latter structures only admix to the former ones and to the ground state via interatomic exchange terms. As we have checked that these triplet-triplet structures do not significantly contribute to the energy they can be omitted.

The atomic orbitals in this case were contracted gaussian type orbitals (GTO's) since our VB program, which has been written for applications to polyatomic molecules [5], is based on the IBMOL-5A integral program [17]. The ls orbital was represented by six primitive GTO's, respectively, were fitted to single-zeta STO quality. The excited 2p and 3d orbitals, composed of two and one primitive GTO's, respectively, were fitted to single-zeta STO's. In earlier calculations [4] we used a contracted set of six GTO's for the 2p orbital but it appeared that all results were exactly the same as those presented in tables 2 and 3 for two GTO's. The atomic orbitals were orthogonalized according to the recipe of ref. [4] since it was demonstrated [4,5] that this type of orthogonalization has very little effect on the van der Waals interaction.

The optimization of the 2p and 3d orbital expo-
ments in order to obtain a minimum VB energy has been performed in separate calculations, since table 2 shows that the contributions of different VB structures to the energy are almost additive, even for distances as small as $R = 5.65$ bohr (near to the van der Waals minimum). This additivity, which holds strictly for the London theory, should be destroyed by charge penetration and exchange effects, but apparently it is hardly affected by the inclusion of such effects. The 2p exponent $\xi_p$ obtained from a maximization of the energy lowering by the “dipole—dipole” VB structures 2, 3 and 4 is equal to 1.30 bohr$^{-1}$, the optimum 3d exponent $\xi_d$ from “dipole—quadrupole” structures 5 to 10 equals 1.45 bohr$^{-1}$, from the “quadrupole—quadrupole” structures 11 to 15 we found $\xi_d = 1.42$ bohr$^{-1}$. Just as in the preceding section (table 1) there is very little difference between the two values for $\xi_d$.

In table 3 we have tabulated the total valence-bond interaction energy $\Delta E_{\text{VB}}$ calculated with the optimized excited state orbitals as a function of the internuclear distance $R$. This is compared, on the one hand with the extensive SCF + Cl calculation by Schaefer et al. [1,2] (basis orbitals 1s, 2s, 3s, 2p, 3p, 3d, 4d, 4f; 346 configurations), on the other hand with the results of the more traditional approach, in which the approximate London energy $\Delta E_L = C_6 R^{-6} + C_8 R^{-8} + C_{10} R^{-10}$ with the optimized values of $C_6$, $C_8$, $C_{10}$ from the preceding section (for the double-zeta 1s orbital) is added to the “first order” valence-bond interaction energy:

$$\Delta E_{\text{VB}}^{(1)} = \langle Y \phi_0^A | H | Y \phi_0^B \rangle - \langle \phi_0^A | H^A | \phi_0^B \rangle.$$  

(2)

The “second-order” valence-bond energy which is also listed in this table, is defined as:

$$\Delta E_{\text{VB}}^{(2)} = \Delta E_{\text{VB}} - \Delta E_{\text{VB}}^{(1)}.$$  

(3)

4. Conclusions

We find that the “effective excited state” model both in the London multipole method and in the VB method yields quite accurate results for the dispersion interactions between two He atoms, as compared with the calculations by Schaefer et al. [1,2]. The mutual agreement between the two methods in the region where charge penetration and exchange effects can be neglected, is also very good. The optimized 2p orbital exponents from the London multipole method (taking the best values obtained with a double-zeta 1s orbital) and from the VB method are very close, the 3d exponents are slightly different. The latter difference could be explained by the fact that the 3d “STO” in VB was actually a single GTO; apparently this fact alone causes little difference in the dispersion energy if the exponent is optimized, but the exponent comparison might not be valid. In any case, the dispersion energy is not very sensitive to the exact form of the excited orbitals (at least in the neighbourhood of the optimum) which was shown by comparing the results for different representations of the 2p orbital (1 STO, 6 GTO, 2 GTO) and the 3d orbital (1 STO, 1 GTO) and for exponent variations in the order of ±0.1 bohr$^{-1}$.

From the previous observations it can be concluded that the use of the London formula (1) with the multipole expansion of $V^{AB}$ gives a valuable procedure for optimizing the excited state orbitals, which can then be substituted in a multistructure valence-bond wavefunction in order to calculate the total van der Waals curve including the repulsive part. This conclusion may be of great practical use for applications to larger systems.

Murrell and Shaw [7] have studied the effect of charge penetration on the London formula by retaining the full interaction operator $V^{AB}$ instead of its multipole expansion. In our VB calculations we have also retained the exact $V^{AB}$ and, moreover, we have included exchange effects in the interaction energy. The effect of exchange on the dispersion energy between two He atoms has been discussed earlier [19–21], but only in more approximate models which are based, for instance, on the Unsöld approximation. Our results show that the deviation from the expanded London formula by the combined effect of charge penetration and exchange at $R = 5.65$ bohr amounts to 4% of the dipole—dipole term in the London energy, 15% of the dipole—quadrupole term and 28% of the quadrupole—quadrupole term. (Murrell and Shaw [7] found a charge penetration contribution to the dipole—dipole term of 3% at $R = 5.6$ bohr.)

The total deviation, which also contains small non-additivity effects, is 8% of the London energy at $R =$
5.65 bohr, 16% at $R = 5.0$ bohr. These figures may be influenced to some extent by the use of orthogonalized atomic orbitals in the VB method. Still, the orthogonalization effects being small also [4,5], we conclude generally that exchange contributions to the dispersion energy are relatively unimportant in the region of the van der Waals minimum. Therefore, one could even ask whether the induction and dispersion energy between larger molecules could not be calculated to a reasonable accuracy by omitting exchange and using the London formula with the "effective excited state" model. The He–He interaction might be a particularly favorable example, however.

Acknowledgement

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References