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 He_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:

$$\Delta E_L^{(2)} = \sum_{k,k'}{}' \frac{|\langle \phi_0^A \phi_0^B | V^{AB} | \phi_k^A \phi_{k'}^B \rangle|^2}{E_0^A - E_k^A + E_0^B - E_{k'}^B}, \qquad (1)$$

where ϕ_k^A, $\phi_{k'}^B$ and E_k^A, $E_{k'}^B$ 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 com-

plete 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 ϕ_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

Table 1

Values of C_6, C_8, C_{10}, $\alpha^{(1)}$, $\alpha^{(2)}$ which are found by optimizing the quantities at the head of each column. All quantities in atomic units. Literature values: Dalgarno and Viktor [13] (for correlated He-atoms): $C_6 = 1.47$, $C_8 = 14.1$, $C_{10} = 63.6$, $\alpha^{(1)} = 1.314$, $\alpha^{(2)} = 2.324$; Schaefer et al. [1,2]: $C_6 = 1.56$, $C_8 = 13.63$; Langhoff et al. [14] (coupled HF): $\alpha^{(1)} = 1.321$, $\alpha^{(2)} = 2.331$; Buckingham and Hibbard [15]: $\alpha^{(1)} = 1.383$, $\alpha^{(2)} = 2.444$

	1s single-zeta			1s double-zeta		
	C_6, C_8 optim.	C_6, C_{10} optim.	$\alpha^{(1)}, \alpha^{(2)}$ optim.	C_6, C_8 optim.	C_6, C_{10} optim.	$\alpha^{(1)}, \alpha^{(2)}$ optim.
ζ_p	1.378	1.378	1.207	1.272	1.272	1.131
ζ_d	1.425	1.443	1.286	1.281	1.293	1.169
$\Delta E_{1s \to 2p}$	1.185	1.185	1.050	1.116	1.116	1.017
$\Delta E_{1s \to 3d}$	1.440	1.460	1.298	1.314	1.325	1.215
C_6	1.127	1.127	1.067	1.543	1.543	1.480
C_8	8.049	8.046	7.616	13.959	13.956	13.386
C_{10} (quad–quad)	27.084	27.102	25.675	59.309	59.330	56.973
Unsöld C_6	1.248	1.248	1.408	1.676	1.676	1.839
C_8	8.906	8.839	9.957	15.099	15.029	16.436
C_{10} (q–q)	29.932	29.526	33.211	63.898	63.352	69.088
$\alpha^{(1)}$	1.126	1.126	1.164	1.358	1.358	1.393
$\alpha^{(2)}$	1.466	1.456	1.503	2.271	2.262	2.315
Unsöld $\alpha^{(1)}$	1.185	1.185	1.337	1.415	1.415	1.554
$\alpha^{(2)}$	1.541	1.520	1.710	2.357	2.337	2.550

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 (1) after expansion of the operator V^{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 $[1s^{A^2}]$ $[1s^{B^2}]$, the excited states in this summation can be written as: $[1s^A \, np_m^A]$ $[1s^B \, n'p_m^B]$. 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 an infinite summation over all products: $[1s^A \, np_m^A][1s^B \, n'd_m^B]$ and $[1s^A \, nd_m^A]$ $[1s^B \, n'p_m^B]$ with $m = 1,0,-1$ and the quadrupole–quadrupole term to a sum over $[1s^A \, nd_m^A]$ $[1s^B \, n'd_m^B]$ 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 np^A and $n'p^B$ 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 cal-
culating the optimized 3d orbital exponent and the
resulting C_8 and C_{10} coefficients. The effective ex-
cited 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 (ζ = 27/16 = 1.6875)
or by a double-zeta STO as given by Clementi [10]
(ζ_1 = 1.44608, c_1 = 0.83415, ζ_2 = 2.86222, c_2 =
0.19060). The monomer transition moments occur-
ring in formula (1) after substituting the multipole
expansion of V^{AB} and the energy levels in the de-
nominator of this formula are easily expressed in the
parameters to be varied: the 2p and 3d orbital expo-
nents. The energy levels were calculated as expecta-
tion 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-elec-
tron energies. The 2p and 3d orbital exponents which
lead to a maximum dispersion energy and the result-
ing C_6, C_8, C_{10} values are given in table 1.

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

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 ap-
proximating the dynamic dipole and quadrupole
polarizabilities $\alpha^{(1)}$ and $\alpha^{(2)}$ of the He atom. We have
calculated the static polarizabilities in a rather analo-
gous way (using expectation values of the exact atom-
ic hamiltonian for the unperturbed energy levels,
whereas Teixeira-Dias and Varandas used the Hartree
one-electron energies) in order to see whether the op-
timized 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" mod-
el, because the latter calculation only requires quanti-
ties 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 polar-
izabilities. Since these quantities do not depend very
sensitively on the exponents, at least in the neighbour-
hood of the optimum, still very reasonable C_6, C_8,
C_{10} values and polarizabilities $\alpha^{(1)}$, $\alpha^{(2)}$ can be ob-
tained 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 reach-
ed by Murrell et al. [7,8] but they found that the
increase from a double-zeta to a five-exponent expan-
sion yielded no further improvement.

The fact that the calculations by the Unsöld approx-
imation, 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 calculat-
ing the transition moment to a single effective ex-
cited state, makes not much difference. One must
realize, though, that the tabulated values for the
Unsöld results were obtained by substituting the ex-
citation energies calculated from the "effective ex-
cited state" model, which cannot be computed direct-
ly. It is striking that these "effective excitation ener-
gies" 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 Unsöld 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, $\sigma + \pi + \delta$)

VB-method			London multipole method	
VB-structure		$\Delta E_{VB}^{(2)}$	$\Delta \widetilde{E}_L^{(2)}$	term
2	$[1s^A 2p_\sigma^A 1s^B 2p_\sigma^B]$	−2.99	−3.16	σ dip–dip
3,4	$[1s^A 2p_\pi^A 1s^B 2p_\pi^B]$	−1.55	−1.58	π dip–dip
σ and π structures (2,3,4)		−4.54	−4.74	$C_6 R^{-6}$
5	$[1s^A 2p_\sigma^A 1s^B 3d_\sigma^B]$	−0.67	−0.80	σ dip-quad
6	$[1s^A 3d_\sigma^A 1s^B 2p_\sigma^B]$			
7,8	$[1s^A 2p_\pi^A 1s^B 3d_\pi^B]$	−0.47	−0.54	π dip–quad
9,10	$[1s^A 3d_\pi^A 1s^B 2p_\pi^B]$			
σ and π structures (5,6,7, 8,9,10)		−1.14	−1.34	$C_8 R^{-8}$
11	$[1s^A 3d_\sigma^A 1s^B 3d_\sigma^B]$	−0.07	−0.09	σ quad–quad
12,13	$[1s^A 3d_\pi^A 1s^B 3d_\pi^B]$	−0.06	−0.08	π quad–quad
14,15	$[1s^A 3d_\delta^A 1s^B 3d_\delta^B]$	−0.01	−0.01	δ quad–quad
σ, π and δ structures (11,12,13,14,15)		−0.13	−0.18	$C_{10} R^{-10}$
all σ structures (2,5,6,11)		−3.68	−4.05	all σ terms
all π structures (3,4,7,8, 9,10,12,13)		−2.08	−2.20	all π terms
all δ structures (14,15)		−0.01	−0.01	all δ terms
all structures		−5.74	−6.26	$C_6 R^{-6} + C_8 R^{-8}$ $+ C_{10} R^{-10}$

Table 3
Interaction energy of He...He (in 10^{-5} atomic units) for various distances (in bohr). The energy contributions are defined in the text

R	$\Delta \widetilde{E}_L^{(2)}$	$\Delta E_{VB}^{(2)}$	$\Delta E_{VB}^{(1)}$ $+ \Delta \widetilde{E}_L^{(2)}$	ΔE_{VB}	ΔE, refs. [1,2]
5.0	−14.06	−11.80	−1.80	+0.46	−1.11
5.2	−10.83	−9.40	−3.41	−1.98	−2.92
5.4	−8.44	−7.54	−3.97	−3.07	−3.66
5.5	−7.48	−6.75	−4.02	−3.29	−3.78
5.6	−6.64	−6.06	−3.96	−3.38	−3.80
5.65	−6.26	−5.74	−3.91	−3.38	−
5.7	−5.92	−5.45	−3.84	−3.37	−3.71
5.8	−5.28	−4.90	−3.67	−3.29	−3.55
6.0	−4.24	−3.98	−3.28	−3.02	−3.21
6.2	−3.43	−3.26	−2.86	−2.69	−
6.5	−2.53	−2.42	−2.28	−2.17	−2.26
6.8	−1.89	−1.83	−1.77	−1.71	−
7.0	−1.57	−1.52	−1.50	−1.45	−1.51
8.0	−0.68	−0.67	−0.67	−0.66	−0.68
9.0	−0.32	−0.32	−0.32	−0.32	−0.33
10.0	−0.16	−0.16	−0.16	−0.16	−0.17
12.0	−0.06	−0.06	−0.06	−0.06	−
14.0	−0.02	−0.02	−0.02	−0.02	−
20.0	−0.00	−0.00	−0.00	−0.00	−

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

$$[1s^{A^2} 1s^{B^2}], [1s^A 2p_m^A 1s^B 2p_m^B], m = 1,0,-1;$$

$$[1s^A 2p_m^A 1s^B 3d_m^B], [1s^A 3d_m^A 1s^B 2p_m^B], m = 1,0,-1;$$

$$[1s^A 3d_m^A 1s^B 3d_m^B], m = 2,1,0,-1,-2.$$

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 1s orbital was represented by six primitive GTO's [18] which, according to the ground state energy, is very near to double-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-

nents 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 ζ_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 ζ_d from "dipole—quadrupole" structures 5 to 10 equals 1.45 $bohr^{-1}$, from the "quadrupole—quadrupole" structures 11 to 15 we found $\zeta_d = 1.42$ $bohr^{-1}$. Just as in the preceding section (table 1) there is very little difference between the two values for ζ_d.

In table 3 we have tabulated the total valence-bond interaction energy ΔE_{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 + CI 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 $\Delta \tilde{E}_L^{(2)} = C_6 R^{-6} + C_8 R^{-8} + C_{10} R^{-10}$ 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:

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

$$- \langle \phi_0^A | H^A | \phi_0^A \rangle - \langle \phi_0^B | H^B | \phi_0^B \rangle . \qquad (2)$$

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

$$\Delta E_{VB}^{(2)} = \Delta E_{VB} - \Delta E_{VB}^{(1)} . \qquad (3)$$

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.

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