Quantum Theoretical Calculations of van der Waals Interactions Between Molecules. Anisotropic Long Range Interactions

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Abstracts

Presenting a relatively simple ab initio method to calculate full van der Waals interaction potentials between molecules, we give rules for the optimization of basis functions which permit the reliable evaluation of second order long range interactions. Closed expressions for the long range interaction energy are derived in which the orientational dependence is simplified to the utmost. Calculations show that even for molecules which have no dipole moment, such as ethylene, the strongly anisotropic electrostatic interactions are of the same magnitude as the dispersion interactions, but also that the anisotropic ("cross") terms in the dispersion energy are about equal in size to the corresponding "quadratic" terms. Even though these anisotropic forces cancel to a large extent in the cohesion energy of the ethylene crystal, they can have important effects on some of the other crystal properties.

1. Introduction

On the experimental side the study of intermolecular forces has for a long time been complicated by the fact that information about these forces had to be...
extracted from various bulk properties, which are ensemble averages [1]. Techniques such as beam scattering [2, 3] and the spectroscopy of van der Waals molecules [4] constitute a significant improvement in this respect. For simple systems, for instance rare gas atoms [5], the collected experimental data have led to the availability of accurate van der Waals potentials. Still, in most cases one has to assume simple parameterized forms of these potentials in order to be able to interpret the experiments. Moreover, the experimental data often do not lead to complete information about the (anisotropic) interactions between molecules.

Another important source of knowledge about van der Waals forces is formed by the semi-empirical methods, usually based on London’s ideas, i.e., the use of first and second order perturbation theory accompanied by a multipole expansion of the interaction operator or a monopole approximation to the charge distribution. Subsequently, experimental quantities, such as polarizabilities or oscillator strengths from optical spectra, are substituted into the resulting expressions, thus yielding accurate values for the long range (induced dipole–induced dipole) interaction coefficient $C_6$ [6]. The experimental properties required to calculate the angular dependence of this coefficient or the values of higher coefficients ($C_8, C_{10}$) are not readily accessible, however.

When using the long range interaction coefficients obtained from semi-empirical methods, but equally those from ab initio calculations [7–10], one should verify, whether they still yield an adequate representation of the interaction in the important region of the van der Waals minimum. Hence a need exists for ab initio calculations of the full van der Waals interaction potentials, especially for molecules, because for those even the long range data are scarce. For that purpose, one can either refine London’s long range theory by taking into account the exchange and charge penetration effects which occur at smaller intermolecular distances, or one can extend the SCF “supermolecule” treatment that is commonly applied at short range. In order to include the dispersion energy, which is an intermolecular correlation effect, the supermolecule treatment must go beyond the independent particle model; in addition, one must separate the intermolecular correlation contributions from the much larger intramolecular correlation energy. The approach we have taken to this problem is to use valence bond type wave functions based on monomer states and, thereby, related to the perturbation scheme; exchange effects are correctly included and the interaction operator is not expanded in a multipole series. This approach permits calculations of van der Waals forces in molecular systems which are somewhat larger than the simple four-electron examples, He-He, He-H$_2$, and H$_2$-H$_2$.

In this paper we describe the main features of this method and illustrate some rules that must be satisfied by the basis functions in order to include the second order long range interactions correctly in the calculations. Furthermore, we concentrate on the occurrence of anisotropic terms in the long range interaction energy and look at the importance of such terms in the ethylene molecular crystal.
2. Method for Calculating van der Waals Interactions. Rules for Choosing the Basis

The valence bond (\(v_b\)) type method we use to calculate van der Waals interaction energies between closed shell molecules \(A\) and \(B\) proceeds by solving a secular problem with wave functions of the type \(Y|k_A\rangle|k_B\rangle\). This secular problem can be solved by standard matrix diagonalization methods (yielding all eigenvalues) up to about 300 \(v_b\) structures, by Nesbet type diagonalizations [11] or by perturbation type methods [12, 13] for much larger problems. The monomer states \(|k_A\rangle\) and \(|k_B\rangle\) are described by single configuration wave functions obtained from molecular scf-lcao calculations. From the ground state \(v_b\) structure \((k_A = 0, k_B = 0)\) we extract the first order electrostatic energy; inclusion of the monomer excited states yields second (and higher) order induction \((k_A = 0, k_B \neq 0 \text{ or } k_A \neq 0, k_B = 0)\) and dispersion \((k_A \neq 0, k_B \neq 0)\) forces. The Young operator \(Y\), which is a spin-free equivalent of antisymmetrization and spin projection [14, 15], ensures that the exchange effects are included in all orders. For large distances the intermolecular effects of \(Y\) vanish and the \(v_b\) results converge asymptotically to the London perturbation theory results [16]. For intermediate distances, including the region of the van der Waals minimum, the orbitals used to construct the monomer wave functions can be orthogonalized without appreciably changing the interaction energy, provided one uses a particular orthogonalization procedure [16, 17] which leaves the first order energy invariant and keeps the virtual orbitals as localized as possible.

The approximation of the monomer states \(|k_A\rangle\) and \(|k_B\rangle\) by single configuration wave functions implies that we neglect the effects of intramonomer correlation on the interaction energy. From calculations on small systems, e.g., He-He around the van der Waals minimum [18], He-H\(_2\) and H\(_2\)-H\(_2\) in the long range limit [10], it can be estimated that those effects do not exceed 10% of the dispersion energy, except in particular cases such as Be-Be, Mg-Mg, Ca-Ca [9], where configuration mixing is known to be substantial already in the monomer ground state.

The excited wave functions \(|k_A\rangle\) and \(|k_B\rangle\) are not chosen to represent physical excited states, corresponding with optical spectra, since this would necessitate the inclusion of continuum states. Instead, we only require for each monomer these excited states to approach a complete set for bound states, together with the ground state wave function. In a very elegant calculation of the leading component \(C_6R^{-6}\) of the long range interaction energy between two hydrogen atoms, using Hylleraas’ variation principle, Hirschfelder and Löwdin [19] have shown how this can be performed. The excited \(2p\), \(3p\), etc., states required to describe the induced dipole-induced dipole interaction were not chosen as the discrete eigenstates of the hydrogen atoms, but rather as a set of orthogonalized Slater-type orbitals with constant exponent [20] equal to the \(1s\)-exponent. Murrell and Shaw [21] have demonstrated that only one excited \(2p\) orbital with an optimized exponent slightly smaller than the \(1s\)-exponent already yields over 99% of the
C₆-value in H₂ and that similar rules apply to the higher (quadrupole) terms, using 3d functions. Similarly, for He-He one obtains rather accurate values for the long range interaction coefficients C₆, C₈, and C₁₀ by taking into account only the lowest single configuration ¹P and ¹D wave functions and then minimizing the second order energy with respect to the 2p and 3d orbital exponents [22, 23]. Inclusion of the excited states so obtained, in a vb calculation [23] yields a van der Waals minimum with 90% of the well depth expected for uncorrelated He atoms [24]. This minimum is in a very good agreement with the experimental well depth [25], since the remaining 10% of the dispersion energy which could be obtained by extending the basis with higher functions, e.g., 4f, is almost canceled by the effect of intramonomer correlations on the interaction energy. (Such a cancellation will always occur to some extent since experience teaches that the monomer correlation tends to weaken the dispersion interactions.)

This procedure of optimizing the nonlinear parameters (atomic orbital exponents) occurring in the monomer excited state wave functions can be extended, in principle, to molecular systems. For the second order perturbation energy, describing the induction and dispersion forces, this optimization can be justified from Hylleraas’ variation principle. The same procedure can also be applied to the corresponding contributions in the vb method. So, for instance, in a vb calculation on He-H₂ [26] we have optimized the exponents of extra 2p and 3d orbitals on hydrogen which were added to the 1s, 2pₓ, and 3dₓ orbitals occurring in the ground state occupied MO in order to construct better molecular polarization functions on H₂ (the virtual MOS from a ground state scf-lcao calculation). The optimum values of the (Slater) exponent of these 2p and 3d orbitals are somewhat smaller than the 1s exponent, just as in the atomic calculations. We illustrate the quality of this AO basis by calculating the dipole polarizability of H₂, which yields: α₀ = 7.08 a.u., α₁ = 4.63 a.u. in good agreement with the experimental data measured at a wavelength of 6328 Å [29] of α₀ = 6.94 a.u., α₁ = 4.82 a.u. Also, we have tested the effective completeness of the basis of Ref. [26] by evaluating the ratio STM/CM (which must of course be one if the basis |k⟩ were complete), where,

\[
\text{STM} = \sum_{k} \langle 0|Q_{l,m}|k⟩\langle k|Q'_{l',m'}|0⟩
\]

(sum over transition moments)

\[
\text{CM} = \langle 0|Q_{l,m}Q_{l',m'}|0⟩ - \langle 0|Q_{l,m}|0⟩\langle Q'_{l',m'}|0⟩
\]

(closure moment)

and Qₘₙ, Q'ₘₙ' are the lowest multipole operators (dipole, quadrupole, octupole) occurring in the expansion of the interaction operator Vₐₗ (see next section). For the dipole operators (l = l' = 1) this yields a ratio STM/CM of 0.999 in the direction parallel to the molecular axis of H₂ and 0.997 in the perpendicular direction.

* We have used a second order formula for the polarizability with state energy differences in the denominator [27], which corresponds closely to the uncoupled Hartree–Fock method b of Ref. [28].
For larger molecules a full optimization of all AO exponents, including those of the atomic polarization functions (e.g., \(2p\) on H, \(3d\) on C and O), would require a considerable amount of computer time, not only if we should perform it in a VB calculation, but even if the long range perturbation formula and the multipole expansion were used. The experience we have gained with smaller systems can be very helpful in the choice of a good basis, however, as we see from the results in Table I where the effective completeness of different AO bases under the dipole operators is compared for the molecules \(\text{C}_2\text{H}_4\) (see also Ref. [27]), \(\text{H}_2\text{O}\), and \(\text{HCOOH}\).

We generally find that the \(\text{CM}\), which are expectation values of the ground state wave functions, do not vary much for the different bases. (They are even more stable than the calculated values of some permanent moments, which are also shown and compared with experimental values in Table I.) The \(\text{STM}\) deviate strongly from the closure moments, however, if the basis is too small (A, B for \(\text{C}_2\text{H}_4\) and A, B, C for \(\text{HCOOH}\)); also for large basis sets which are not appropriately chosen (C for \(\text{C}_2\text{H}_4\) and D for \(\text{HCOOH}\)) the deviations are still

**Table I.** Completeness test under the dipole operators. Tabulated is the ratio \(\text{STM}/\text{CM}\) as defined by formula (1), on the basis of tesseral harmonics: \(x = 2^{-1/2}(Q_{1,1} + Q_{1,-1}), y = i(2^{-1/2}(Q_{1,1} + Q_{1,-1}),\) and \(z = Q_{1,0}\).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Lowest permanent moment</th>
<th>STM/CM; in parentheses: (\text{CM(a.u.)}^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ethylene</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basis sets:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Split valence</td>
<td>(-2.74)</td>
<td>(0.77(9.79))</td>
</tr>
<tr>
<td>B. Double zeta (DZ)</td>
<td>(-2.73)</td>
<td>(0.74(9.78))</td>
</tr>
<tr>
<td>C. DZ + pol. f. (SCF optimized)</td>
<td>(-2.74)</td>
<td>(0.88(9.58))</td>
</tr>
<tr>
<td>D. DZ + pol. f. (polarizability optimized)</td>
<td>(-2.55)</td>
<td>(0.96(9.74))</td>
</tr>
<tr>
<td><strong>Formic acid</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basis sets:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A. Minimal</td>
<td>0.59</td>
<td>(0.50(10.13))</td>
</tr>
<tr>
<td>B. Split valence</td>
<td>0.65</td>
<td>(0.67(10.49))</td>
</tr>
<tr>
<td>C. Double zeta (DZ)</td>
<td>0.72</td>
<td>(0.65(10.73))</td>
</tr>
<tr>
<td>D. DZ + pol. f. (SCF optimized)</td>
<td>0.78</td>
<td>(0.87(10.41))</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extended basis set (double pol. f. on O, single pol. f. on H)</td>
<td>0.81</td>
<td>(0.95(4.34))</td>
</tr>
</tbody>
</table>

\(^a\) Definition of coordinate system: for ethylene the origin is in the middle of the CC bond, the \(y\)-axis is directed along CC; for formic acid the origin is in the center of mass, the \(x\)-axis is directed parallel to the HC bond; for water the origin is at the O atom, the \(x\)-axis is directed along the OH bond; in all cases the \(z\)-axis is perpendicular to the molecular plane. The very small nondiagonal (\(x, y\)) terms, appearing for water and formic acid, have been omitted from this table.

\(^b\) Basis sets from Ref. [27] (ethylene), Ref. [30] (formic acid), and Ref. [31] (water).

\(^c\) Experimental value of the quadrupole moment component \(Q_{2,0}\) for ethylene: \(-2.75\) a.u. [32].

Experimental values of the dipole moment \(\langle \mu \rangle\) (defined by \(\langle \mu \rangle = (Q_{1,0} - 2Q_{1,1}Q_{1,-1})^{1/2}\)): 0.55 a.u. for formic acid [33], 0.73 a.u. for water [34].
substantial. We have found similar results for the higher moment operators. So, we conclude that the completeness of the molecular ground state plus excited state wave functions depends strongly on the $\text{AO}$ basis. Just as in the $\text{H}_2$ molecule and the $\text{He}$ and $\text{H}$ atoms, atomic polarization functions must be included in the basis with exponents somewhat smaller than the valence orbital exponents, in order to calculate reliable second order quantities. For ethylene, again, this conclusion is supported by the calculated values of the molecular polarizabilities. For example, the dipole polarizability tensor calculated with basis $D$ yields [27]:

\[
\alpha_{xx} = 26.5 \text{ a.u.}, \quad \alpha_{yy} = 41.1 \text{ a.u.}, \quad \alpha_{zz} = 23.2 \text{ a.u.}
\]

in good agreement with the experimental values [35]:

\[
\alpha_{xx} = 26.1 \text{ a.u.}, \quad \alpha_{yy} = 36.4 \text{ a.u.}, \quad \alpha_{zz} = 23.0 \text{ a.u.}
\]

The van der Waals potential between two ethylene molecules we have, as yet, only calculated by the $\text{vb}$ method in the smaller basis $A$ [16]; the long range interactions (electrostatic, induction, and dispersion) have already been evaluated in all bases [27] and more extensive $\text{vb}$ calculations are in progress.

3. Long Range Interactions and their Anisotropy

When the distance between the interacting systems becomes so large that we can neglect exchange and penetration of their charge distributions, the main contributions to the interaction energy can be obtained from the well known London perturbation formulas. Usually the calculation of this energy is simplified by expanding the interaction in a multipole series. When expressing the multipole moments in spherical harmonics $Y_{l,m}$ [36],

\[
Q_{l_A,m_A}(r_A) = \left[ \frac{4\pi}{2l_A + 1} \right]^{1/2} \sum_i Z_i Y_{l_A,m_A}(\hat{r}_i)
\]

and using the irreducible tensor formalism [37], a closed formula for the expansion of the interaction energy in powers of the distance $R$ can be obtained [38]. This formula is also very suitable to study the dependence of the energy on the orientations of the interacting molecules. In expression (2) the summation over $i$ runs over all particles in molecule $A$ with charges $Z_i$ and coordinates $r_i = (\hat{r}_i, \hat{r}_i)$ in a local system of axes. The irreducible tensor product between two sets of tensors $Q_{l_A} = \{Q_{l_A,m_A} | m_A = -l_A, \ldots, l_A\}$ and $Q_{l_B} = \{Q_{l_B,m_B} | m_B = -l_B, \ldots, l_B\}$ is defined by [37]

\[
[Q_{l_A} \otimes Q_{l_B}]_m = \sum_{m_A,m_B} Q_{l_A,m_A} Q_{l_B,m_B}(l_A, m_A; l_B, m_B | l, m)
\]

where $(l_A, m_A; l_B, m_B | l, m)$ is a Clebsch–Gordan coefficient. The multipole expansion of the interaction $V_{AB}$ between two charge clouds A and B connected...
by the vector $\mathbf{R} = (R, \hat{R})$, pointing from A to B, then becomes

$$V^{AB} = \sum_{l_A=0}^{\infty} \sum_{l_B=0}^{\infty} C_{l_A,l_B} R^{-l_A-l_B-1} \sum_{m=-l_A-l_B}^{l_A+l_B} (-1)^m Y_{l_A+l_B,-m}(\hat{R})$$

$$\times [Q_{l_A}(\mathbf{r}_A) \otimes Q_{l_B}(\mathbf{r}_B)]_{l_A+l_B}^{l_A+l_B}$$

(4)

with

$$C_{l_A,l_B} = (-1)^l \left[ \frac{4\pi}{2l_A+2l_B+1} \right]^{1/2} \left( \frac{2l_A+2l_B}{2l_A} \right)^{1/2}$$

where the multipole moments on A and B are first coupled to a tensor of maximum order $l_A + l_B$, which is then coupled with the geometrical factor $Y_{l_A+l_B,-m}(\hat{R})$ to a scalar. A very short derivation of formula (4) has been given in Ref. [15].

The quantum mechanical first order electrostatic interaction energy between molecules is directly obtained from the classical interaction formula (4) by interpreting the multipole moments $Q_{l_A}(\mathbf{r}_A)$ and $Q_{l_B}(\mathbf{r}_B)$ as operators and taking their expectation values: $\langle 0_A | Q_{l_A} | 0_A \rangle$ and $\langle 0_B | Q_{l_B} | 0_B \rangle$. When the molecules A and B are rotated around their local origins over Euler angles $\omega_A = (\alpha_A, \beta_A, \gamma_A)$ and $\omega_B = (\alpha_B, \beta_B, \gamma_B)$ the variation of the first order energy is expressed by

$$\Delta E^{(1)}(\mathbf{R}, \omega_A, \omega_B) = \sum_{l_A=0}^{\infty} \sum_{l_B=0}^{\infty} C_{l_A,l_B} R^{-l_A-l_B-1} \sum_{m=-l_A-l_B}^{l_A+l_B} (-1)^m$$

$$\times Y_{l_A+l_B,-m}(\hat{R}) \langle 0_A | Q_{l_A} | 0_A \rangle \cdot \mathbf{D}^{\omega_A}(\omega_A^{-1}) \otimes \langle 0_B | Q_{l_B} | 0_B \rangle \cdot \mathbf{D}^{\omega_B}(\omega_B^{-1}) Y_{l_A+l_B}^{l_A+l_B}$$

(5)

where $\mathbf{D}^{\omega}(\omega)$ is the matrix representing $\omega$ in the $(2l+1)$-dimensional irreducible representation of the rotation group $so(3)$ [36]. This first order energy is strongly anisotropic; it can change sign upon rotation of the monomers. It follows immediately from the orthogonality relation in $so(3)$,

$$\frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{\pi} \int_0^{2\pi} D^\alpha(\alpha \beta \gamma)^\ast_D(\alpha \beta \gamma)_{mm'} d\alpha \sin \beta d\beta d\gamma = \delta_{m0}\delta_{m'0}\delta_{l0}$$

(6)

that it vanishes when averaged (with equal weight) over all orientations of one of the subsystems, except when this subsystem carries a charge (monopole moment).

The multipole expansion of the second order (induction and dispersion) energy reads as follows:

$$\Delta E^{(2)}(\mathbf{R}) = \sum_{l_A,l_B} \sum_{l_{A1},l_{B1}} C_{l_A,l_B} C_{l_{A1},l_{B1}} R^{-l_A-l_B-l_{A1}-l_{B1}-2}$$

$$\times \sum_{k_A,k_B=0}^{l_A,l_B} (E_{0A} - E_{k_A} + E_{0B} - E_{k_B})^{-1} \sum_{m=-l_A-l_B}^{l_A+l_B} \sum_{m'=-l_{A1}-l_{B1}}^{l_{A1}+l_{B1}} (-1)^{m+m'}$$

$$\times Y_{l_A+l_B,-m}(\hat{R}) Y_{l_{A1}+l_{B1},-m}(\hat{R}) \langle 0_A | Q_{l_A} | k_A \rangle \otimes \langle 0_B | Q_{l_B} | k_B \rangle Y_{l_{A1}+l_{B1}}^{l_{A1}+l_{B1}}$$

$$\times \langle k_A | Q_{l_A} | 0_A \rangle \otimes \langle k_B | Q_{l_B} | 0_B \rangle Y_{l_{A1}+l_{B1}}^{l_{A1}+l_{B1}}$$

(7)
Although the rotational dependence of $\Delta E^{(2)}$ can actually be derived from formula (7) by substitution of the rotation matrices $D^I(\omega)$, just as in the first order energy Eq. (5), the resulting expression then becomes a rather complicated function of $\omega_A$ and $\omega_B$ [39]. A simplification is obtained by expanding the product of the two spherical harmonics dependent on $\hat{R}$ in a Gaunt series and expressing the product of the two tensors, each composed of two transition moments, in irreducible products. The latter operation yields an expansion in fourfold tensor products, which can be further simplified by the following recoupling scheme, which is also physically appealing because it expresses the second order energy as an interaction between just two tensors localized on the subsystems. First couple the transition moments (considered as irreducible tensors) on monomer A together and also those on monomer B; then couple the resulting monomer tensors. This yields, after some algebra [15] and substitution of the rotation matrices, an expression for the second order energy in which the simplification of the rotational dependence is pushed to its limits:

$$\Delta E^{(2)}(\mathbf{R}, \omega_A, \omega_B) = (4\pi)^{1/2} \sum_{l_A,l'_A l_B,l'_B} (-1)^{l_B+l'_B}$$

$$\times A(l_A, l'_A, l_B, l'_B) R^{-l_A-l'_A-l_B-l'_B-2} \sum_{L_A,L_B} B(l_A, l'_A, L_A; l_B, l'_B, L_B; L)$$

$$\times \sum_{k_A,k_B} (E_{0_A} - E_{k_A} + E_{0_B} - E_{k_B})^{-1} \sum_M (-1)^M Y_{L,-M}(\hat{R})$$

$$\times \left[ \langle 0_A | Q_{l_A} | k_A \rangle \otimes \langle k_A | Q_{l_A} | 0_A \rangle \right]^{L_A} \cdot D^{L_A}(\omega_A^{-1})$$

$$\otimes \left[ \langle 0_B | Q_{l_B} | k_B \rangle \otimes \langle k_B | Q_{l_B} | 0_B \rangle \right]^{L_B} \cdot D^{L_B}(\omega_B^{-1})$$

(8)

in which

$$L_A = |l_A - l'_A|, \ldots, l_A + l'_A$$

$$L_B = |l_B - l'_B|, \ldots, l_B + l'_B$$

$$L = |L_A - L_B|, \ldots, L_A + L_B$$

$$M = -L, \ldots, +L$$

and

$$A(l_A, l'_A, l_B, l'_B) = \left[ \frac{(2l_A + 2l_B + 1)!(2l'_A + 2l'_B + 1)!}{2l_A!2l_B!2l'_A!2l'_B!} \right]^{1/2}$$

$$B(l_A, l'_A, L_A; l_B, l'_B, L_B; L) = \left[ \frac{(2L_A + 1)(2L_B + 1)}{2L + 1} \right]^{1/2} (l_A + l_B, 0; l'_A + l'_B, 0|L, 0)$$

$$\times \left\{ \begin{array}{ccc}
    l_A & l'_A & L_A \\
    l_B & l'_B & L_B \\
    l_A + l_B & l'_A + l'_B & L \\
  \end{array} \right\}$$

where the expression between curly brackets is the Wigner 9 – j symbol [40]. Note that the “moments” on A and B having order $L_A$ and $L_B$, respectively, are
coupled to all possible $L$-values. This is different from the first order energy where the monomer moments are coupled to maximum $L$-value only. So, the second order energy can not be given a classical interpretation of interacting mutually induced moments.

When this result for the second order energy is averaged over all $\omega_A$ and $\omega_B$ it follows easily, as in first order, that only the contributions with $L_A = 0$ and $L_B = 0$ remain. These contributions arise only from the so-called quadratic terms [41] in the second order energy ($l_A = l'_A; l_B = l'_B$). The cross terms with $l_A \neq l'_A$ or $l_B \neq l'_B$ can change sign upon rotation and average out. If we substitute the expression for the rotationally averaged transition moments,

$$T_{0k}^{(l)} = (2l + 1)^{-1} \sum_{m=-l}^{+l} |\langle 0| Q_{l,m} |k \rangle|^2$$

the average second order energy becomes [15]

$$\langle \Delta E^{(2)}(R) \rangle = \sum_{l_A,l_B} \left( \frac{2l_A + 2l_B}{2l_A} \right) R^{-2l_A-2l_B-2} \times \sum'_{k_A,k_B} (E_{0A} - E_{kA} + E_{0B} - E_{kB})^{-1} T_{0A,kA}^{(l_A)} T_{0B,kB}^{(l_B)}$$

which is simpler than the corresponding expression derived by Riera and Meath [39, formula (31)]. Actually, the lowest term ($l_A = l_B = 1$) in formula (10) has the same appearance as the simple London formula for the induced dipole–induced dipole interaction between atoms. So, our derivation forms a proof that the London formula and its generalization to higher moments are equally applicable to the interactions between arbitrary, freely rotating molecules.

These averaging characteristics of the anisotropic interaction energies are very important for the properties of nonideal gases (liquids) where the molecules do rotate more or less freely. In a $(1/kT)$ expansion of the second virial coefficient [42], the electrostatic energy, contrary to the second order interactions, does not contribute to the linear term. Therefore, the contribution of the electrostatic forces, although these are often larger (when not averaged) than the induction or dispersion forces, is generally dominated by the latter [43].

Also in molecular crystals, the anisotropic interactions may cancel to some extent, even though the motions of the molecules about their equilibrium positions are mostly small. This is because a given molecule usually sees neighbors with many different orientations. We have studied the importance of the anisotropic interactions in a system of two ethylene molecules [27] and, also, in the ethylene molecular crystal [44].

In Table II one can observe that the electrostatic energy in the ethylene dimer is comparable in size to the dispersion energy (the induction energy is much smaller) and therefore forms a strong anisotropic component in the ethylene–ethylene interaction. The second order cross terms have the same magnitude as the quadratic terms arising in the same power of $R$ and, for this reason, the
### Table II

Coefficients in the $R^{-1}$ expansion of the first and second order interaction energy for the ethylene dimer, calculated from LCAO-SCF wave functions on the monomers. The electrostatic coefficient $C_{r,n} = (l_r, l_n)$ represents the interaction between a permanent $2^r_n$ multipole on molecule $A$ and a permanent $2^r_n$ multipole on $B$. Similar definitions apply to the induction and dispersion coefficients.

<table>
<thead>
<tr>
<th>Electrostatic$^b$</th>
<th>Geometry I</th>
<th>Geometry II</th>
<th>Isotropic$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6(2A, 2B)$</td>
<td>(a.u. x $10^4$)</td>
<td>450.8</td>
<td>-240.4</td>
</tr>
<tr>
<td>$C_7(2A, 4B) + C_7(4A, 2B)$</td>
<td>(a.u. x $10^1$)</td>
<td>-158.3</td>
<td>101.9</td>
</tr>
<tr>
<td>$C_9(2A, 6B) + C_9(6A, 2B)$</td>
<td>(a.u. x $10^3$)</td>
<td>31.9</td>
<td>4.0(=13.4-9.4)</td>
</tr>
<tr>
<td>$C_9(4A, 4B)$</td>
<td>(a.u. x $10^3$)</td>
<td>27.2</td>
<td>-16.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Induction$^b$</th>
<th>Geometry I</th>
<th>Geometry II</th>
<th>Isotropic$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6(1A, A, 2B) + C_6(2A, 1B, 1B)$</td>
<td>(a.u. x $10^2$)</td>
<td>-13.5</td>
<td>-14.0(=-2.0-12.0)</td>
</tr>
<tr>
<td>$C_{10}(2A, 2A, 2B) + C_{10}(2A, 2B, 2B)$</td>
<td>(a.u. x $10^4$)</td>
<td>-3.7</td>
<td>-3.4(=-0.7-2.7)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dispersion$^b$, quadratic</th>
<th>Geometry I</th>
<th>Geometry II</th>
<th>Isotropic$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6(1A, A, 1B, 1B)$</td>
<td>(a.u.)</td>
<td>-340.8</td>
<td>-394.6</td>
</tr>
<tr>
<td>$C_6(1A, A, 2B) + C_6(2A, 1B, 1B)$</td>
<td>(a.u. x $10^2$)</td>
<td>-117.9</td>
<td>-164.2(=-97.9-66.3)</td>
</tr>
<tr>
<td>$C_{10}(2A, 2A, 2B, 2B)$</td>
<td>(a.u. x $10^4$)</td>
<td>-21.1</td>
<td>-30.1</td>
</tr>
<tr>
<td>$C_{10}(1A, A, 2B, 2B) + C_{10}(3A, 3A, 1B, 1B)$</td>
<td>(a.u. x $10^4$)</td>
<td>-26.1</td>
<td>-35.5(=-21.4-14.1)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dispersion$^c$, cross$^c$</th>
<th>Geometry I</th>
<th>Geometry II</th>
<th>Isotropic$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_8(1A, A, 1B, 3B) + C_8(1A, 3A, 1B, 1B)$</td>
<td>(a.u. x $10^2$)</td>
<td>109.3</td>
<td>8.8(=-72.5+63.7)</td>
</tr>
<tr>
<td>$C_{10}(1A, A, 3A, 2B)$</td>
<td>(a.u.)</td>
<td>-4.6</td>
<td>6.2</td>
</tr>
<tr>
<td>$C_{10}(1A, 3A, 1B, 3B)$</td>
<td>(a.u. x $10^4$)</td>
<td>27.3</td>
<td>67.1</td>
</tr>
<tr>
<td>$C_{10}(2A, 2A, 1B, 3B) + C_{10}(1A, 3A, 2B, 2B)$</td>
<td>(a.u. x $10^4$)</td>
<td>30.0</td>
<td>6.1(=-20.0+26.1)</td>
</tr>
</tbody>
</table>

---

* In geometry I the two molecules have their corresponding symmetry axes parallel and coinciding $z$-axes. Geometry II can be obtained from I by rotating one of the molecules over 90° around its $x$-axis. The isotropic value is obtained by averaging over all orientations [formula (10)].

* The electrostatic energy has been computed in basis set C, the induction and dispersion terms in basis set D [27].

* In $C_{10}$ the nonzero cross terms arising from $(11,15)$ and $(11,24)$ interactions are lacking.

---

Anisotropy in the second order contributions is dominated by these terms, rather than by the orientational dependence of the quadratic terms.

The isotropic long range interactions calculated with the orientationally averaged formula (10) can be compared with the experimental value $C_6 = 599.6$ a.u. obtained from viscosity data [45]. The experimental $C_6$, which describes the long range part of a Lennard–Jones potential, should be considered as an effective $C_6$ which, in fact, also contains higher ($C_8$, $C_{10}$) contributions. The isotropic induction and dispersion energy calculated, for instance, at $R = 10$ a.u., with the average $C_6$, $C_8$, $C_{10}$ from Table II is 64.63 $\times 10^{-5}$ a.u., in rather good agreement with the experimental result, 59.96 $\times 10^{-5}$ a.u.

Table III shows that, indeed, in the ethylene crystal the anisotropic terms, both in first and second order, cancel to a large extent in the cohesion energy. Preliminary lattice dynamics calculations at our institute by Wasiutynski have shown, though, that these anisotropic terms do have significant effects on the phonon modes in the crystal, particularly on the librational modes. Therefore, they may strongly influence specific crystal properties, for instance, the tendency...
TABLE III. Lattice energy contributions (in 10^-3 a.u.) for the ethylene crystal ("b-structure" [46]), computed as a sum of dimer interactions, employing basis B in Unsold's approximation [44].

<table>
<thead>
<tr>
<th>Summation range (a.u.)</th>
<th>in parentheses: number of molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>R=7.82</td>
<td>R=8.59</td>
</tr>
<tr>
<td>(2)</td>
<td>(8)</td>
</tr>
</tbody>
</table>

Electrostatic

<table>
<thead>
<tr>
<th>C_6(2,2)R^-</th>
<th>C_7(2,4)R^+</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.43</td>
<td>-1.12</td>
<td>-0.11</td>
</tr>
<tr>
<td>0.25</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>0.68</td>
<td>-0.98</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Induction

<table>
<thead>
<tr>
<th>C_6(11.2)R^- + C_10(22,2)R^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.04</td>
</tr>
</tbody>
</table>

Dispersion

<table>
<thead>
<tr>
<th>C_6(11,11)R^-</th>
<th>C_6(11,22)R^-</th>
<th>C_6(11,13)R^- (cross)</th>
<th>C_10(22,22)R^-</th>
<th>C_10(11,33)R^-</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.52</td>
<td>-3.37</td>
<td>-0.51</td>
<td>-0.50</td>
<td>-0.33</td>
<td>-0.25</td>
</tr>
<tr>
<td>-1.25</td>
<td>-2.14</td>
<td>-0.27</td>
<td>-0.15</td>
<td>-0.06</td>
<td>-0.02</td>
</tr>
<tr>
<td>-0.10</td>
<td>0.03</td>
<td>0.07</td>
<td>&lt;-0.01</td>
<td>&lt;-0.01</td>
<td>&lt;&lt; 0.01</td>
</tr>
<tr>
<td>-0.47</td>
<td>-0.62</td>
<td>-0.07</td>
<td>-0.02</td>
<td>-0.01</td>
<td>&lt;-0.01</td>
</tr>
<tr>
<td>-0.60</td>
<td>-0.73</td>
<td>-0.09</td>
<td>-0.03</td>
<td>-0.01</td>
<td>&lt;-0.01</td>
</tr>
<tr>
<td>-3.94</td>
<td>-6.83</td>
<td>-0.87</td>
<td>-0.70</td>
<td>-0.41</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

* Including both (A, B) and (B, A) interactions.

to undergo orientational order–disorder transitions, as observed for ethylene at high pressures [47].

Finally we remark that our results in Refs. [16], [27], and [44] indicate that the multipole expansion, in first as well as in second order, starts to diverge for ethylene at a distance which is only slightly smaller than the crystal nearest-neighbor distance. For crystals built of larger molecules such as pyrazine the multipole expansion breaks down already for the nearest-neighbors [44]. Therefore, when one evaluates van der Waals potentials, for application to molecular crystal calculations, charge penetration (and exchange) effects should be included, at least for the first shell of neighbors. Hence, we are pursuing the vb type calculations, as described in Section 2, for which the information about the basis set optimization and the anisotropy of the long range interactions presented in this paper is very useful.

Acknowledgment

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Bibliography


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