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A New Method for Approximate Estimates of the Dispersion Interaction Between Two Molecules

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A new method to evaluate the dispersion interaction between two weakly interacting closed shell molecules is presented. The method is based on a second-order sum-over-states perturbation method, where the nominator is approximated by products of one electron integrals.

Key words: Dispersion interaction – Van der Waals molecules – Perturbation estimates.

1. Introduction

In the last years a few methods for determining the dispersion interaction between two molecules have been proposed. In one approach the dispersion energy is estimated by a second-order sum-of-states perturbation method [1–8]. In this approximation the dispersion energy (positive for stabilization) is given by

$$E_{\text{disp}} = \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{vac}} \frac{|\langle A_0 B_0 | H^1 | A_{i\to k} B_{\mu\to\nu}\rangle|^2}{E_{i_{\text{A}}\to k_{\text{A}},\mu_{\text{B}}\to\nu_{\text{B}}} - E_0} \tag{1}$$

where A_0B_0 is the Hartree product of the Hartree–Fock wavefunction for the molecules A and B, $A_{i\to k}B_{\mu\to\nu}$ is the corresponding Hartree product for singly excited states of A and B, H^1 is the molecular interaction part of the Hamiltonian. E_0 is the sum of the unperturbed energies for molecules A and B and $E_{i_{\text{A}}\to k_{\text{A}},\mu_{\text{B}}\to\nu_{\text{B}}}$ is the sum of the energies corresponding to the singly excited wavefunctions $A_{i\to k}$ and $B_{\mu\to\nu}$. More rigorous estimates of the dispersion energies based on configuration interaction calculations have only been made in a few cases for other systems than monoatomic gases [9–14]. Together with these *ab initio* calculations also some semi-empirical estimates of the dispersion energy have been made [15–17]. In this work a method to evaluate the dispersion energy is presented. The method is based on Eq. (1) but the nominator is approximated by products of one-electron integrals.

2. Theory

Starting with Eq. (1) and using a Möller–Plesset partition and canonical Hartree–Fock SCF orbitals one obtains:

$$E_{\text{disp}} = 4 \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{vac}} \frac{|\langle i_{\text{A}}(1)k_{\text{A}}(1)|1/r_{12}|\mu_{\text{B}}(2)\nu_{\text{B}}(2)\rangle|^2}{e_k - e_i + e_\nu - e_\mu} \tag{2}$$

where the nominator is a two-electron integral over the canonical SCF orbitals i_{A}, k_{A}, μ_{B} and ν_{B} and the denominator is the difference of the orbital energies. If $1/r_{12}$ is expanded in a Taylor series in $\boldsymbol{r}_1$, $\boldsymbol{r}_2$ and $\boldsymbol{R}_{12}$ accoring to Fig. *1* and remembering the orbital orthogonality one obtains

$$\begin{aligned}
&\langle i_{\text{A}}(1)k_{\text{A}}(1)\left|\frac{1}{r_{12}}\right|\mu_{\text{B}}(2)\nu_{\text{B}}(2)\rangle \\
&\approx \frac{1}{R_{12}^3}\,(\langle i_{\text{A}}|\boldsymbol{r}_1|k_{\text{A}}\rangle\cdot\langle\mu_{\text{B}}|\boldsymbol{r}_2|\nu_{\text{B}}\rangle - \frac{3}{R^2}\langle i_{\text{A}}|\boldsymbol{r}_2\cdot\boldsymbol{R}_{12}|k_{\text{A}}\rangle \\
&\quad\cdot\langle\mu_{\text{B}}|\boldsymbol{r}_2\cdot\boldsymbol{R}_{12}|\nu_{\text{B}}\rangle) \\
&\quad+\frac{3}{2R_{12}^5}(\langle i_{\text{A}}|r_1^2 k_{\text{A}}\rangle\cdot\langle\mu_{\text{A}}|\boldsymbol{r}_2\cdot\boldsymbol{R}_{12}|\nu_{\text{B}}\rangle - \langle i_{\text{A}}|\boldsymbol{r}_1\cdot\boldsymbol{R}_{12}|k_{\text{A}}\rangle\cdot\langle\mu_{\text{B}}|r_2^2|\mu_{\text{B}}\rangle \\
&\quad+2(\langle i_{\text{A}}|\boldsymbol{r}_1\boldsymbol{r}_1\cdot\boldsymbol{R}_{12}|k_{\text{A}}\rangle\cdot\langle\mu_{\text{B}}|\boldsymbol{r}_2|\mu_{\text{B}}\rangle - \langle i_{\text{A}}|\boldsymbol{r}_1|k_{\text{A}}\rangle\cdot\langle\mu_{\text{B}}|\boldsymbol{r}_2\boldsymbol{r}_2\cdot\boldsymbol{R}_{12}|\nu_{\text{B}}\rangle) \\
&\quad-\frac{5}{R_{12}^2}(\langle i_{\text{A}}|\boldsymbol{r}_1\cdot\boldsymbol{R}_{12}\boldsymbol{r}_1\cdot\boldsymbol{R}_{12}|k_{\text{A}}\rangle\cdot\langle\mu_{\text{B}}|\boldsymbol{r}_2\cdot\boldsymbol{R}_{12}|\nu_{\text{B}}\rangle \\
&\quad-\langle i_{\text{A}}|\boldsymbol{r}_1\cdot\boldsymbol{R}_{12}|k_{\text{A}}\rangle\langle\mu_{\text{B}}|\boldsymbol{r}_2\cdot\boldsymbol{R}_{12}\boldsymbol{r}_2\cdot\boldsymbol{R}_{12}|\nu_{\text{B}}\rangle)+\cdots.
\end{aligned} \tag{3}$$

If Eq. (3) is used in Eq. (2), an approximate value of the dispersion energy may be calculated. There is however one arbitrary parameter in Eq. (3). That is, when dealing with polyatomic molecules there is no obvious choice of origin for r_1 and r_2. The dispersion energy is however not very sensitive to this parameter if r_1 and $r_2 \ll R_{12}$ and in this work the ambiguity is removed by calculating the center of charge for each orbital. Then the origin of the transition dipole and quadrupole is taken as the average value of the center of charge of the two orbitals

$$\boldsymbol{r}_{i\to k} = \tfrac{1}{2}(\boldsymbol{r}_i + \boldsymbol{r}_k)\,. \tag{4}$$

Further it should be noted that since the perturbation calculation is taken only to second order, the result depends on the energy denominator in the perturbation expansion. In the work by Kochanski *et al.* on the H_2 dimer [2] the dispersion

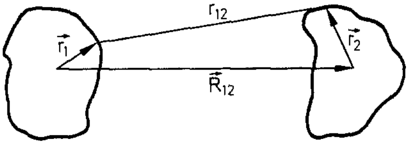

Fig. 1. Definition of $\boldsymbol{r}_1$, $\boldsymbol{r}_2$, r_{12} and $\boldsymbol{R}_{12}$ for two interacting molecules

energy calculated using Epstein–Nesbet partition is 30% larger than the value calculated using Möller–Plesset partition. The value obtained from converged CI calculations is usually in between [9]. In this work two different energy denominators have been used. The first choice corresponds to an ordinary Möller–Plesset partition and the second choice is a modified version of the Möller–Plesset partition that will be justified below. At the SCF level the polarisability may be calculated either using finite perturbation theory (i.e. adding a term corresponding to an electrical field to the Fock matrix and performing an ordinary SCF calculation) or in the uncoupled Hartree–Fock approximation (i.e. perform a first order perturbation calculation on the molecule using the electrical field as perturbation operator). The expression for one component of the polarisability tensor in the uncoupled HF approximation is then given by

$$P_{xx'} = \sum_{i,k} \frac{\langle i|x|k\rangle\langle i|x'|k\rangle}{e_k - e_i}. \tag{5}$$

This polarisability is usually too small compared to the more accurate value obtained in an ordinary finite perturbation calculation. This gives a possibility to scale the orbital energies in Eq. (5) so that the scaled uncoupled Hartree–Fock polarisability is equal to the finite perturbation theory value. If only the dipole–dipole interaction part of the dispersion interaction is considered, the dispersion energy may be written

$$E_{\text{disp}} = 4 \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{vac}} \frac{1}{R_{12}^6} \times \frac{(\langle i_A|\boldsymbol{r}_1|k_A\rangle \cdot \langle \mu_B|\boldsymbol{r}_2|\nu_B\rangle - 3/R_{12}^2 \langle i_A|\boldsymbol{r}_1 \cdot \boldsymbol{R}_{12} \,|\, k_a\rangle \cdot \langle \mu_B|\boldsymbol{r}_2 \cdot \boldsymbol{R}_{12}|\nu_B\rangle)^2}{e_k + e_\nu - e_i - e_\mu} \tag{6}$$

or if the Z-axis is taken as the internuclear axis

$$E_{\text{disp}} = 4 \sum_{i}^{\text{occ}} \sum_{k}^{\text{vac}} \sum_{\mu}^{\text{occ}} \sum_{\nu}^{\text{vac}} \frac{1}{R_{12}^6} \times \frac{(\langle i_A|x_1|k_A\rangle\langle \mu_B|x_2|\nu_B\rangle + \langle i_A|y_1|k_A\rangle\langle \mu_B|y_2|\nu_B\rangle - 2\langle i_A|z_1|k_A\rangle\langle \mu_B|z_2|\mu_B\rangle)^2}{e_k + 4_\nu - e_i - e_\mu}. \tag{7}$$

From Eq. (7) it may be seen that the dispersion energy expression is built up from terms similar to those giving the polarisability. Consequently it seems resonable to scale the orbital energies in the dispersion energy calculation with the same scaling factor that was obtained by putting the uncoupled Hartree–Fock polarisability equal to the finite perturbation theory value. In this work the scaling factor has been obtained by putting the traces of the two polarisability tensors equal.

3. Test Calculations

The main advantage of an approximate method like the one described here lies in its computational simplicity – this will be discussed further in the next paragraph – but its value depends strongly on its predicted abilities. Since accurate estimates of

Table 1. Dispersion interaction for the H_2 dimer energy in 10^{-3}a.u.

Geometry	d a.u.	This work Möller–Plesset	This work Energy-scaled	Ref. [3] Möller–Plesset	Ref. [3] Nesbeth–Epstein	Ref. [9][a] All singles and doubles
Rectangular	4	2.5735	3.4560	1.6251	2.2943	
	5	0.6064	0.8143	0.5101	0.7320	
	5.5	0.3304	0.4437	0.2961	0.4270	0.400
	6	0.1907	0.2561	0.1768	0.2558	0.243
	6.5	0.1154	0.1550	0.1089	0.1579	0.152
	7	0.0726	0.0975	0.0692	0.1006	0.097
	7.5	0.0473	0.0635	0.0452	0.0660	0.064
	10	0.0080	0.0108	0.0078	0.0114	0.011
	20	0.00012	0.00016	0.00012	0.00017	
T-shape	4	3.3711	4.5271	2.2761	3.1648	
	5	0.7686	1.0322	0.7148	1.0161	
	5.5	0.4138	0.5557	0.4126	0.5908	0.491
	6	0.2364	0.3175	0.2438	0.3509	0.297
	6.5	0.1419	0.1906	0.1481	0.2139	0.182
	7	0.0888	0.1193	0.0927	0.1342	0.115
	7.5	0.0575	0.0772	0.0598	0.0867	0.073
	10	0.00961	0.0129	0.0098	0.0143	0.009
	20	0.00141	0.000189	0.00014	0.00021	
Linear	4	4.7751	6.4126	3.6332	4.9808	
	5	1.0600	1.4235	1.1377	1.6027	
	5.5	0.5650	0.7580	0.6517	0.9269	0.726
	6	0.3201	0.4299	0.3807	0.5447	0.452
	6.5	0.1908	0.2562	0.2270	0.3270	0.283
	7	0.1186	0.1593	0.1393	0.2015	0.181
	7.5	0.0764	0.1026	0.0881	0.1279	0.118
	10	0.0126	0.0169	0.0135	0.0197	0.018
	20	0.00018	0.00024	0.00018	0.00027	
Non-planar	4	2.3630	3.1733	1.4453	2.0428	
	5	0.5656	0.7596	0.4637	0.6662	
	5.5	0.3099	0.4162	0.2720	0.3925	0.384
	6	0.1796	0.2412	0.1639	0.2375	0.232
	6.5	0.1091	0.1465	0.1017	0.1475	0.144
	7	0.0689	0.0925	0.0651	0.0945	0.091
	7.5	0.0450	0.0604	0.0428	0.0622	0.060
	10	0.00772	0.01037	0.0075	0.0109	0.010
	20	0.000116	0.000156	0.00011	0.00017	

[a] A slightly larger basis set has been used.

the dispersion energy based on perturbation energy are very time-consuming only a few exist. Below, examples will be given which show how this method reproduces these more accurate results.

3.1. The Dimers of H_2 and Ne

In two articles Kochanski *et al.* have studied the H_2 dimer [29], where several different basis sets have been used. The dispersion interactions have been

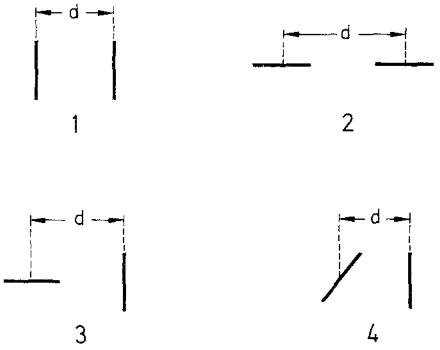

Fig. 2. Different orientations of the H_2 dimer. (1) Rectangular, (2) Linear, (3) T-shape, (4) Non-planar

estimated using three different methods. The first estimates made by Kochanski is based on Eq. (2), the second is a slightly modified form of Eq. (2) where a Nesbeth–Epstein partition has been used, and the third is based on conventional CI calculations including all singly and doubly replaced configurations [18]. Unfortunately the same basis set has not been used for all three methods. Estimates of the dispersion energy for the four different configurations studied (see Fig. 2) for different intermolecular distances are given in Table 1. It should be noted that the same basis set (called B3 in [2], i.e. a 4s, 3p basis contracted to 2s, 3p) is used for the first four columns of Table 1, but the fifth estimate made by ordinary CI calculations is made with a slightly larger basis set giving an approximately 5% larger dispersion energy.

From Table 1 it may be seen for intermolecular distances where the overlap is small the agreement between the two Möller–Plesset estimates of the dispersion energy is good (i.e. the error is of the order of 10%). As may be expected the error is larger for small intermolecular distances and decreases with increasing intermolecular distances It is also gratifying that the agreement between the energy-scaled estimate and the estimate based on all single and double CI calculations are quite satisfactory. Results very similar to those obtained for the H_2 dimer are also obtained for Ne_2 (see Table 2). The same basis set has been used in this study, ((10, 6, 4) [8, 6, 4], for further information see Ref. [7]), and in the reference study of Prisette [7], whereas the value of Stevens [15] is obtained with a larger Slater basis, which could be expected to include more of the dispersion interaction. Here it is more difficult to make comparisons, but considering that the dispersion energy

Table 2. Dispersion interaction for the Ne dimer energy in 10^{-3} a.u.

d a.u.	This work Möller–Plesset	Energy scaled	Ref. [7] Nesbeth–Epstein	Ref. [15] CI
5	0.3739	0.4370	0.493	
5.5	0.2051	0.2397	0.271	
6	0.1191	0.1392	0.156	0.166
6.1136	0.1059	0.1238	0.139	
6.5	0.0724	0.0846	0.094	

Table 3. Dispersion energy for the H_2O dimer in 10^{-3} a.u.

Distance (Å)	This work Möller–Plesset	Energy scaled	Ref. [10] CI
2.7	0.2618	0.3245	0.2350
2.8	0.2022	0.2505	0.1949
2.9	0.1579	0.1956	0.1634
3.0	0.1246	0.1544	0.1388
3.1	0.0994	0.1232	0.1192

calculated using Möller–Plesset partition are usually smaller than the values obtained using Nesbeth–Epstein partition and remembering that the value from a CI calculation including all singles and doubles usually falls in between and also remembering that a basis set giving larger dispersion energy has been used in the CI calculation, the agreement is quite satisfactory.

3.2. *The Dimers of H_2O and HF*

The molecules used for test calculations in the previous section were very small non-polar molecules. Consequently it may also be interesting to see how the proposed method works for large polar systems. Unfortunately no accurate dispersion energy calculations for such systems are available, but a few accurate studies of the somewhat larger water and HF dimers exist [10–11, 14]. In Table 3 the dispersion energies obtained with this method are compared with the more accurate values calculated using all singly and doubly replaced states in a conventional CI calculation [10]. The same basis set (11, 7, 1) [5, 3, 1] is used for 0 and (5, 1) [3, 1] for H, see Ref. [10] for further data. For a description of the geometry see Fig. 3. The conclusions to be drawn from Table 3 are again the same: for large intermolecular distances where the overlap is small both methods are in good agreement with more accurate estimates and for smaller intermolecular distances the error increases. It is however encouraging to see that even at the minimum of the intermolecular potential, which occurs at 2.924 Å, the result differs only by 10–20% from the more reliable CI calculations.

A similar analysis is made for a linear head-to-tail conformation of the HF dimer. Reference data are taken from a study of Lischka, and a basis set of (11, 7, 2) [7, 4, 2] for F and (6, 1) [4, 1] for H is used. In the reference study Gaussian lobe functions have been used but in this work Cartesian functions are used. This should, however, not effect the results significantly.

In Table 4 the obtained values are shown. Here the situation is quite different. The agreement between the contribution from the configuration interaction calculations to the binding energy differs drastically from the calculated dispersion

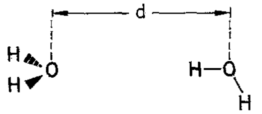

Fig. 3. Geometry of the studied water dimer

Table 4. Dispersion energy for the HF-dimer in 10^{-3} a.u.

	This work		Ref. [11]					
			Total interaction			Inter molecular part		
F–F distance	Möller–Plesset	Energy scaled	IEPA	CEPA	PNO-CI	IEPA	CEPA	PNO-CI
5.0	2.516	3.081	−0.423	−0.160	0.162	2.452	2.177	2.176
5.5	1.147	1.405	−0.333	−0.148	0.057	1.282	1.133	1.133
6.0	0.594	0.727	−0.309	−0.164	−0.018	0.697	0.613	0.613
8.0	0.084	0.103	−0.265	−0.188	−0.118	0.095	0.082	0.082
12.0	0.006	0.007	−0.117	−0.085	−0.063	0.007	0.006	0.006

energy. The explanation is given by Lischka in his work. In the three columns to the right Lischka's estimate of the dispersion binding energy is given. These columns agree well with the estimates made in this work. However, when performing CI calculations on the HF monomer, the properties of this molecule change drastically, leading to a change in e.g. electrostatic and exchange interactions in the HF dimer.

4. Discussion

In the previous paragraph it was shown that for molecular complexes where the electrostatic and polarisability properties of the monomers do not change significantly due to configuration interaction calculations, the effect of a configuration interaction calculation may be accurately estimated with the proposed method. Here it should also be pointed out that the change in electrostatic and polarisation interactions due to configuration interaction effects in the monomers may be fairly accurately estimated using ordinary electrostatic theory and performing configuration interaction calculations on the monomers. It is also worth noting that when the change in electrostatic interaction is of the same order of magnitude as the dispersion energy, the dispersion energy is usually small compared to the total interaction energy.

As mentioned before, the main advantage with this method is its computational simplicity. One point on the H–F dimer surface took 5 hours on a Univac 1108 in the work of Lischka. Most of this time was spent in the program steps needed to evaluate the correlation contribution to the binding energy. An estimate of the dispersion interaction with an ordinary sum-over-states second-order perturbation approach may be estimated to take half an hour. A calculation of the dispersion energy with the proposed method takes a few seconds.

One further advantage of the proposed method compared to ordinary CI calculations is that the calculated total dispersion energy is size consistent whereas ordinary CI calculations underestimate the dispersion interaction. This may explain why the energy-scaled dispersion interaction is somewhat larger than the ordinary CI value for larger intermolecular distances for large systems.

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