

Ab initio Calculation of Intermolecular Dispersion Energy and Induction Energy of Nitramide Dimer

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The dispersion energies, induction energies and their exchange counterparts (exchange-dispersion and exchange-induction energies) between two interacting nitramide molecules at several separations are derived based upon symmetry-adapted perturbation theory (SAPT). The results show that (1) the effect of intramonomer electron correlation on dispersion energies and induction energies for nitramide dimer system is remarkable especially in the region near the van der Waals minimum distance (0.42 nm). (2) At smaller separations the dispersion energies and the induction energies are largely quenched by their exchange counterparts, and this case in induction interaction is much more remarkable than in dispersion interaction. (3) Since at shorter distances there exists the strong short-range interaction due to electron transfer which quickly decays and even disappears at larger separations, the two different R -dependency formulae of induction energies were found: one is *ca.* $R^{-12.7}$ at short distances, and the other *ca.* $R^{-7.0}$ at large separations. The latter R -dependency is similar to that (*ca.* $R^{-7.2}$) of dispersion. (4) In the case of strong polar interaction existing in nitramide dimer, the “true” induction correlation terms of higher order than ${}^tE_{\text{ind}}^{(22)}$ may be important.

Keywords dispersion energy, induction energy, nitramide dimer, symmetry-adapted perturbation theory

Introduction

In these years there has been considerable interest in the *ab initio* evaluation of intermolecular interaction in energetic systems.¹⁻⁴ These calculations are all based upon a supermolecular method in which the interaction energy is defined as

$$E_{\text{int}} = E_{\text{AB}} - (E_{\text{A}} + E_{\text{B}}) \quad (1)$$

However, sometimes it is necessary to calculate the physically interpretable contributions to the E_{int} such as electrostatic, repulsion, induction and dispersion energies, especially in investigating the interaction mechanisms and developing the accurate force field parameters of these energetic systems. Since nitramide ($\text{NO}_2\text{-NH}_2$) is a prototype of important explosives like 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), it is often chosen as a model compound to theoretically understand nature of these explosives.¹ Here we first concentrate upon dispersion energy and induction energy of the nitramide dimer.

Computational methods

In symmetry-adapted perturbation theory (SAPT),⁵ the interaction energy can be expressed as

$$E_{\text{int}} = E_{\text{pol}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{pol}}^{(2)} + E_{\text{exch}}^{(2)} + \dots \quad (2)$$

where, the subscript “pol” and “exch” are the abbreviation for polarization and exchange, respectively. The $E_{\text{pol}}^{(1)}$ and $E_{\text{exch}}^{(1)}$ are the classical electrostatic interaction and the result of the resonance tunnelling of electrons between interacting systems, respectively. The second-order polarization energy $E_{\text{pol}}^{(2)}$ can be subdivided into the induction and dispersion interactions as

$$E_{\text{pol}}^{(2)} = E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)} \quad (3)$$

$E_{\text{disp}}^{(2)}$ and $E_{\text{ind}}^{(2)}$ are further expanded in W_{A} and W_{B} as

$$E_{\text{disp}}^{(2)} = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} E_{\text{disp}}^{(2mn)} \quad (4)$$

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$$E_{\text{ind}}^{(2)} = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} E_{\text{ind}}^{(2mn)} \quad (5)$$

where W_X is the intramonomer (intramolecular) correlation operator of molecule X, m and n indicate the orders in W_A and W_B , respectively. $E_{\text{disp}}^{(20)}$ and $E_{\text{ind}}^{(20)}$ represent the dispersion and induction energies between two interacting "Hartree Fock" molecules without any intramonomer correlation. The corrections $E_{\text{disp}}^{(2k)}$ and $E_{\text{ind}}^{(2k)}$ with $k > 0$ ($k = m + n$) reflect intramonomer correlation effects.

In this work, the $E_{\text{disp}}^{(20)}$ and $E_{\text{ind}}^{(20)}$ for the nitramide dimer will be derived using Sum-Over-States (SOS)⁶

$$E_{\text{disp}}^{(20)} = \sum_{a>0} \sum_{b>0} \frac{\langle \Phi_0^A \Phi_0^B | V \Phi_a^A \Phi_b^B \rangle}{\epsilon_0^A + \epsilon_0^B - \epsilon_a^A - \epsilon_b^B} \quad (6)$$

$$E_{\text{ind}}^{(20)} = \sum_{a>0} \frac{\langle \Phi_0^A \Phi_0^B | V \Phi_a^A \Phi_0^B \rangle}{\epsilon_0^A - \epsilon_a^A} + \sum_{b>0} \frac{\langle \Phi_0^A \Phi_0^B | V \Phi_0^A \Phi_b^B \rangle}{\epsilon_0^B - \epsilon_b^B} \quad (7)$$

In the above two expressions, V is intermolecular interaction operator,⁵ and Φ_x^X and ϵ_x^X (when $x > 0$, it stands for excitation states, and in the case that $x = 0$, it is for ground state) are Hartree Fock (HF) determinants and orbital energies. It is noted that the V operator is expressed here in complete form and not as a multipole expansion. This means that the charge overlap effects are properly taken into consideration and thus the Eq. (6) and Eq. (7) are both well defined for all intermolecular distances. It is clear that the two SOS energies do not account for any intramonomer correlation effects at all.

To consider the intramonomer correlation effects in the nitramide dimer system, the correlated dispersion energy ($E_{\text{disp}}^{(2)}$) through the 2nd order in $W_A + W_B$

(i.e., $E_{\text{disp}}^{(2)}(2) = \sum_{k=0}^2 E_{\text{disp}}^{(2k)}$) will be calculated according to the theoretical expressions⁷ for the $E_{\text{disp}}^{(2)}$ developed by Rybak *et al.*

Each correction $E_{\text{ind}}^{(2k)}$ can be decomposed as⁵

$$E_{\text{ind}}^{(2k)} = {}^a E_{\text{ind}}^{(2k)} + {}^t E_{\text{ind}}^{(2k)} \quad (8)$$

where ${}^a E_{\text{ind}}^{(2k)}$ and ${}^t E_{\text{ind}}^{(2k)}$ denote the "apparent" and "true" correlation contributions to the induction energy. Since $E_{\text{ind}}^{(2)}(c)$ of the induction energy which can be obtained from Coupled Hartree Fock (CHF) theory has been contained in HF interaction energy from supermolecular method and $E_{\text{ind}}^{(2)}(c) = \sum_{l=0}^{\infty} {}^a E_{\text{ind}}^{(2l)}$,⁵ the "true"

contributions are these quantities that represent the proper intramonomer correlation effects. Thus, a large part of the intramonomer correlation contributions to $E_{\text{ind}}^{(2)}$ is already included in the $E_{\text{ind}}^{(2)}(c)$. To our

knowledge, only theoretical expression for ${}^t E_{\text{ind}}^{(22)}$ was developed.⁸ By the way, ${}^t E_{\text{ind}}^{(21)} = 0$.⁹

In this work, the CHF dispersion energy ($E_{\text{disp}}^{(2)}(c)$) using polarization propagator theory^{10,11} will be also derived.

As a matter of fact, there exist the couplings of the electron exchange with dispersion interaction and induction interaction, and correspondingly, the two couplings are interpreted as exchange-dispersion energy and exchange-induction. The two exchange energies constitute the $E_{\text{exch}}^{(2)}$, i.e.,

$$E_{\text{exch}}^{(2)} = E_{\text{exch-ind}}^{(2)} + E_{\text{exch-disp}}^{(2)} \quad (9)$$

The theoretical expression for the exchange-dispersion energy ($E_{\text{exch-disp}}^{(20)}$) used in this dimer system can be found in the paper by Rybak *et al.*⁷ It was proposed by Sadlej that the exchange-induction energy ($E_{\text{exch-ind,resp}}^{(20)}$) with response effect could be evaluated using CHF theory.¹² The "resp" means response effect. The explicit orbital expressions for the two exchange energies are too complex to write out here.

The most stable dimer (see Figure 1) available for this work was found from its possible stable dimer geometries derived by counterpoise (CP)¹³ corrected optimization at MP2/6-311G(d,p) level. This CP corrected optimization was carried out by the modified Gaussian 94 code.¹⁴ The vibration analysis shows that there are no virtual (negative) frequencies for these possible stable dimers including the most stable one. The intermolecular distance R is a distance between the centers of mass (COM) of the interacting nitramide monomers. The R for the most stable dimer is 0.42 nm. The structural parameters for this most stable nitramide dimer are listed in Table 1.

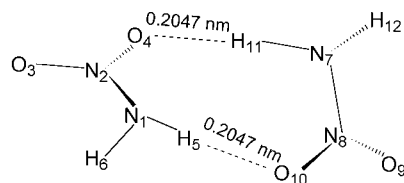


Figure 1 The most stable geometry of nitramide dimer.

Based upon these computational methods, $E_{\text{disp}}^{(2)}$, $E_{\text{disp}}^{(20)}$, $E_{\text{ind}}^{(20)}$, $E_{\text{disp}}^{(2)}(c)$, $E_{\text{ind}}^{(2)}(c)$, ${}^t E_{\text{ind}}^{(22)}$, $E_{\text{exch-disp}}^{(20)}$ and $E_{\text{exch-ind,resp}}^{(20)}$ at several intermolecular separations from $R = 0.32$ nm to 1.42 nm were calculated. The way of changing R is by translating one of nitramide monomers along the line through two COM of the two monomers, and in this process the both monomers keep rigid and their orientation described by the dihedral angle of 131.7° between N(1)-N(2) and N(7)-N(8) is fixed too.

In this work, aug-cc-pvDz basis functions plus 3s2p1d mid-functions (MC+BS)¹⁵ were used in each single point calculation. The HF orbitals and orbital

Table 1 The internal geometrical parameters for monomer A(B) of the most stable nitramide dimer

N2(8)—N1(7)	0.1383
O3(9)—N2(8)	0.1222
O4(10)—N2(8)	0.1231
H5(11)—N1(7)	0.1019
H6(12)—N1(7)	0.1013
O3(9)-N2(8)-N1(7)	117.3
O4(10)-N2(8)-N1(7)	116.5
H5(11)-N1(7)-N2(8)	110.1
H6(12)-N1(7)-N2(8)	109.3
O4(10)-N2(8),N1(7)-O3(9)	126.0
H5(11)-N1(7),N2(8)-O3(9)	-153.6
H6(12)-N1(7),N2(8)-H5(11)	115.7

energies for nitramide monomers were obtained from ATMOL,¹⁶ which would be input into a suite of routines¹⁷ from Szalweicz to compute $E_{\text{disp}}^{(2)}(2)$, $E_{\text{disp}}^{(20)}$, $E_{\text{ind}}^{(20)}$, ${}^tE_{\text{ind}}^{(22)}$, $E_{\text{exch-disp}}^{(20)}$ and $E_{\text{exch-ind,resp}}^{(20)}$. $E_{\text{ind}}^{(2)}(c)$ and $E_{\text{disp}}^{(2)}(c)$ were obtained by solving a set of linear equations¹⁸ which were incorporated into a special CHF code by Alston.

The percentage for the intramonomer correlation part (represented by the difference, $E_{\text{disp}}^{(2)}(2) - E_{\text{disp}}^{(20)}$) of $E_{\text{disp}}^{(2)}(2)$ was evaluated by

$$\eta = \frac{E_{\text{disp}}^{(2)}(2) - E_{\text{disp}}^{(20)}}{E_{\text{disp}}^{(2)}(2)} \times 100\% \quad (10)$$

Results and discussions

Table 2 collects the results in this work. It is shown

Table 2 The R -dependent dispersion and induction energies and their exchange counterparts (R in nm, energy in kJ/mol)

R	Dispersion parts				Induction parts				
	$E_{\text{disp}}^{(20)}$	$E_{\text{disp}}^{(2)}(c)$	$E_{\text{disp}}^{(2)}(2)$	$E_{\text{exch-disp}}^{(20)}$	$E_{\text{ind}}^{(20)}$	$E_{\text{ind}}^{(2)}(c)$	${}^tE_{\text{ind}}^{(22)}$	$E_{\text{exch-ind,resp}}^{(20)}$	${}^tE_{\text{exch-ind}}^{(22)}$ ^a
0.32	-171.039	-171.064	-173.603	34.902	-563.868	-669.938	-74.979	397.699	44.510
0.36	-71.526	-65.776	-77.317	14.269	-125.261	-151.595	-20.852	94.581	13.010
0.37	-57.744	-53.597	-63.229	10.925	-87.315	-106.118	-14.978	64.356	9.083
0.395	-34.215	-32.311	-38.475	5.362	-36.872	-45.217	-6.453	24.116	3.442
0.42	-20.701	-19.718	-23.710	2.515	-16.614	-20.495	-2.718	8.903	1.181
0.47	-8.181	-7.754	-9.501	0.507	-4.255	-5.238	-0.436	1.214	0.101
0.57	-1.780	-1.605	-2.018	0.018	-0.648	-0.767	0.015	0.024	-4.79×10^{-4}
0.72	-0.334	-0.285	-0.365	1.127×10^{-4}	-0.107	-0.121	0.007	8.257×10^{-5}	-5.023×10^{-6}
0.92	-0.066	-0.054	-0.071	8.315×10^{-7}	-0.020	-0.022	0.002	5.823×10^{-7}	-4.197×10^{-8}
1.17	-0.014	-0.012	-0.015	1.311×10^{-8}	-0.004	-0.004	3.35×10^{-4}	1.311×10^{-8}	0
1.42	-0.004	-0.003	-0.005	0	-0.001	-0.001	1.006×10^{-4}	0	0

^a see Eq. (15).

that both dispersion energies and induction energies are more negative (attractive) as intermolecular separation decreases, and at the separation of over 1.17 nm the both energies and their exchange counterparts all are very small and may be neglected.

However, it was found that the dispersion and induction energies have different characteristics of R -dependency. The R -dependency of $E_{\text{disp}}^{(2)}(2)$ agrees to a considerable degree (correlation coefficient is 0.999) with the formula of $-CR^{-7.2}$. As we know, the most frequent approaches in empirical atom-atom potentials of dispersion parts, like Buckingham "exp-6" and Lennard-Jones "12-6", adopt $-CR^{-6}$ term to describe the dispersion interaction between interacting molecules. This difference is mainly caused by the penetration effects which have been taken into account by $E_{\text{disp}}^{(2)}(2)$.

By contrast, R -dependency of the correlated induction energy evaluated by $(E_{\text{ind}}^{(2)}(c) + {}^tE_{\text{ind}}^{(22)})$ has two different stages. The R -dependency in the region (0.32 nm to 0.47 nm) near the minimum distance is very different from that in the range from 0.57 nm to 1.42 nm. The R -dependency ($\propto R^{-12.7}$) of the correlated induction energies in the former region takes on an obvious characteristic of short-range interaction. This fact may be due to relatively strong electronic transfer in this region. At the distance of over 0.57 nm the R -dependency ($\propto R^{-7.0}$) of the correlated induction energies is similar to that ($\propto R^{-7.2}$) of $E_{\text{disp}}^{(2)}(2)$. This suggests that at these separations the short-range interaction factor from the electronic transfer is very weak and even disappears.

As compared with the $E_{\text{disp}}^{(2)}(2)$ accounting for the intramonomer correlation effects, the $E_{\text{disp}}^{(2)}(c)$ based upon CHF is not satisfactory in numerical results. However, the CHF scheme was found to be able to speed by a factor of more than 10. Therefore, an effort to compute the dispersion energy from the Coupled

Kohn-Sham (CKS) method¹⁸ is being made by us. For larger systems than nitramide dimer, at present there exist barriers in the CKS method involved mainly in theoretical defects of present conventional DFTs. Asymptotic correction techniques are being introduced to override these defects and it is believed that the CKS scheme will be applied to these larger systems in the near future.

Figure 2 displays the evaluation of the effect of correlation parts on dispersion energies in the range of intermolecular distances from 0.32 to 1.42 nm. It is very obvious that at van der Waals minimum distance of 0.42 nm, the intramonomer correlation effect arrives up to maximum ($\eta=13.9\%$). And it is clear that even at these distances over 11.7 angstroms, η is still more than 6%. Since the total dispersions at these distances tend to be very small, these correlation parts can be disregarded. These facts suggest that in the region near the van der Waals minimum distance, the intramonomer correlation effects on dispersion energies have to be taken into account.

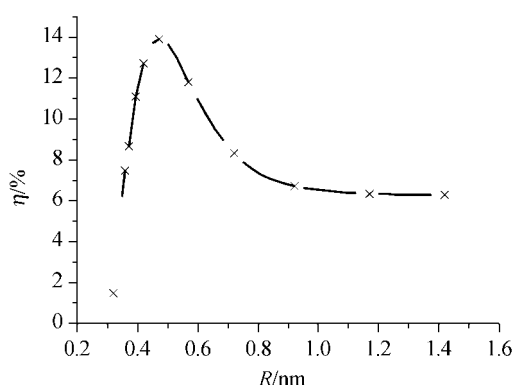


Figure 2 The evaluation of intramonomer correlation effects of dispersion at intermolecular separations.

It is also shown in the Table 2 that in the region near 0.42 nm, the ${}^tE_{\text{ind}}^{(22)}$ values are substantial quantities, some of which are over 10% of $E_{\text{ind,resp}}^{(20)}$ and near the total sum of apparent correlation corrections, that is, the difference ($E_{\text{ind}}^{(2)}(\text{c}) - E_{\text{ind}}^{(20)}$). These substantial quantities are partly due to the fact that there may exist remarkable electronic transfer between nitramide molecules. It follows from these figures and facts that in the case of polar interaction existing in such system as nitramide dimer even higher order (in correlation) terms may be quite important.

The $E_{\text{exch-ind,resp}}^{(20)}$ and $E_{\text{exch-disp}}^{(20)}$ in the Table 2 illustrate that at shorter intermolecular distances the induction energy is much more severely quenched by the exchange-induction effect than the dispersion done by the exchange-dispersion effect. As already mentioned, in this situation of nitramide dimer system the induction

correlations at smaller separations are significant due possibly to strong electron transfer. So, it is necessary to include the exchange quenching of ${}^tE_{\text{ind}}^{(22)}$. The theoretical framework to compute this correction has not been developed until now and one may estimate its value by scaling $E_{\text{exch-ind,resp}}^{(20)}$ using the known values of ${}^tE_{\text{ind}}^{(22)}$ and $E_{\text{ind}}^{(2)}(\text{c})$.

$${}^tE_{\text{exch-ind}}^{(22)} \approx E_{\text{exch-ind,resp}}^{(20)} \frac{{}^tE_{\text{ind}}^{(22)}}{E_{\text{ind}}^{(2)}(\text{c})} \quad (11)$$

The sum, $E_{\text{exch-disp}}^{(20)} + E_{\text{exch-ind,resp}}^{(20)} + {}^tE_{\text{exch-ind}}^{(22)}$, quickly decays in the formula of $31044700e^{-3.46R}$. This means that the exchange-dispersion interaction and exchange-induction interaction are important physical origins of repulsive force at shorter distances. The sum is an important correlation part of exchange energy in this nitramide dimer.

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