



On the role of higher-order correlation effects on induction interactions between closed-shell molecules

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Introduction

Symmetry-adapted perturbation theory (SAPT) [1] is a useful tool for calculating interaction energies of van der Waals molecules. The SAPT interaction energy is

- **BSSE-free** and
- can be interpreted in terms of **physically meaningful** components, such as first-order electrostatic ($E_{\text{elst}}^{(1)}$), second-order induction ($E_{\text{ind}}^{(2)}$), second-order dispersion ($E_{\text{disp}}^{(2)}$) terms and their exchange counterparts: first-order exchange ($E_{\text{exch}}^{(1)}$), exchange-induction ($E_{\text{exch-ind}}^{(2)}$), and exchange-dispersion ($E_{\text{exch-disp}}^{(2)}$).

In most cases, exact wave functions of monomers are not known. Usually, SCF monomer determinants are used as the zeroth-order approximation to the monomers' wave functions and the monomer fluctuation operators become the additional perturbations. This leads to the Møller-Plesset (MP) expansion of SAPT corrections.

Motivation

The induction energy is the major second-order contribution to the interaction energy of the polar monomers. However, even for the case of nonpolar molecules, the short-range induction energy should be included in any quantitative description of intermolecular interactions.

Two types of the MP expansions of the induction energy were proposed:

- the nonrelaxed expansion [2] – a simple application of the MP partitioning of monomer Hamiltonians, the orbital response is not taken into account,
- the relaxed expansion [3] – an additional term is added to the monomer fluctuation operator, so that the orbital relaxation is accounted for in each order:

$$E_{\text{ind}}^{(2)} = \sum_{n=0}^{\infty} E_{\text{ind,resp}}^{(2n)} \quad (1)$$

The convergence of both expansions was not investigated so far. Some time ago, Olsen and collaborators [4] showed that similar correlation expansions for the dipole moment are strongly divergent. Given the fact that in the multipole approximation the MP expansions of the dipole moment and of the induction energy are closely related, one may expect that the MP expansion of the induction energy will be divergent as well. Therefore, the aim of this work is

- to present nonperturbative alternatives for the calculation of the correlation part of the induction energy;
- to compare the MP induction energy calculated up to the second order in terms of the fluctuation operator, $E_{\text{ind,resp}}^{(22)} = E_{\text{ind,resp}}^{(220)} + E_{\text{ind,resp}}^{(202)}$, with the induction energy obtained by those nonperturbative methods;
- to identify other possible missing factors in the SAPT energy.

Method

We consider the interaction of two closed-shell monomers A and B. The expression for the energy of the induction interaction between A and B, $E_{\text{ind}}^{(2)}$, is obtained from the second-order Rayleigh-Schrödinger perturbation theory of intermolecular forces (polarization theory). It can be written as a sum of terms corresponding to the polarization of the monomer A by the electrostatic field of the monomer B (Ω_B), $E_{\text{ind}}^{(2)}(A \leftarrow B)$, and vice versa:

$$E_{\text{ind}}^{(2)} = E_{\text{ind}}^{(2)}(A \leftarrow B) + E_{\text{ind}}^{(2)}(B \leftarrow A). \quad (2)$$

The component $E_{\text{ind}}^{(2)}(A \leftarrow B)$ is given by:

$$E_{\text{ind}}^{(2)}(A \leftarrow B) = \left(\frac{\partial^2 \mathcal{E}_A(\zeta)}{\partial \zeta^2} \right)_{\zeta=0}, \quad (3)$$

where $\mathcal{E}_A(\zeta)$ is the lowest eigenvalue of the Hamiltonian $H_A + \zeta \Omega_B$.

The operator Ω_B is defined by the equations:

$$\Omega_B = \sum_{i=1}^{N_B} \omega_B(\mathbf{r}_i), \quad (4)$$

$$\omega_B(\mathbf{r}_i) = u_B(\mathbf{r}_i) + \int \rho_B(\mathbf{r}_j) \frac{1}{r_{ij}} d\mathbf{r}_j, \quad (5)$$

where $\rho_B(\mathbf{r})$ is the electron density of the monomer B, and $u_B(\mathbf{r}_i)$ describes the interaction between the electron i of the monomer B and the nuclei of the monomer A.

In the present work we will consider an approximation to $E_{\text{ind}}^{(2)}$ obtained by replacing in Eq. (3) the exact energies and in Eq. (5) the exact electron densities, by the approximate energies and electron densities obtained from

- the CCSD method (relaxed),
- the CCSD method (nonrelaxed),
- the QCISD method (relaxed).

E.g. for the CCSD method we have

$$E_{\text{ind}}^{(2)}(\text{CCSD}) = \left(\frac{\partial^2 \mathcal{E}_A^{\text{CCSD}}(\zeta)}{\partial \zeta^2} \right)_{\zeta=0} + \left(\frac{\partial^2 \mathcal{E}_B^{\text{CCSD}}(\zeta)}{\partial \zeta^2} \right)_{\zeta=0}, \quad (6)$$

where $\mathcal{E}_A^{\text{CCSD}}(\zeta)$ and $\mathcal{E}_B^{\text{CCSD}}(\zeta)$ are the CCSD energies of the monomer A and B, respectively, computed with the perturbed Hamiltonians $H_A + \zeta \Omega_B^{\text{CCSD}}$ and $H_B + \zeta \Omega_A^{\text{CCSD}}$, respectively. The operators Ω_B^{CCSD} and Ω_A^{CCSD} were obtained from Eqs. (4)–(5) with the electron densities $\rho_A(\mathbf{r})$ and $\rho_B(\mathbf{r})$ approximated by their CCSD expressions. It can be shown that $E_{\text{ind}}^{(2)}(\text{CCSD})$ is exact to the third-order in the intramonomer correlation, and sums up a specific class of diagrams (single, double, and disconnected quadruple excitation diagrams) to infinite order.

To investigate the convergence of the expansion (1) we will compare the induction energy computed through the second order:

$$E_{\text{ind}}^{(2)}(2) = E_{\text{ind,resp}}^{(20)} + E_{\text{ind,resp}}^{(22)}, \quad (7)$$

with $E_{\text{ind}}^{(2)}(\text{method})$. Thus, the difference,

$$\Delta_{\text{ind}}^{(2)}(\text{method}) = E_{\text{ind}}^{(2)}(\text{method}) - E_{\text{ind}}^{(2)}(2), \quad (8)$$

represents the contribution of the third and higher-order SDQ diagrams to the second-order induction energy. The term $E_{\text{ind,resp}}^{(220)}$ was calculated by using in Eq. (3) the MP2 energy of the monomer A and in Eq. (5) the SCF electron density of the monomer B.

The intermolecular interaction energy $E_{\text{int}}^{\text{SAPT}}$ was represented by the sum of the first- and second-order polarization and exchange contributions:

$$E_{\text{int}}^{\text{SAPT}} = E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{exch-def}}^{(2)} + E_{\text{exch-disp}}^{(2)}. \quad (9)$$

Technical details

The SAPT calculations were performed with the SAPT program [5]. The coupled-cluster electrostatic correction and induction terms, as well as the supermolecular CCSD(T) energies were obtained using the Molpro package [6], utilizing analytical MP2, CCSD, and QCISD electron densities available in this package [7–9]. The densities were used for the construction of Ω_X operators (Eqs. (4)–(5)). Then the finite-field calculations with the Ω_X perturbing field were performed in order to obtain the induction energy. The field strength of 0.005 was used.

We have performed calculations for several van der Waals complexes:

1. two polar molecules: $(\text{HF})_2$ and $(\text{H}_2\text{O})_2$,
2. two nonpolar molecules: $(\text{CO})_2$ and $(\text{N}_2)_2$,
3. a rare gas atom and a polar molecule: $\text{He-H}_2\text{O}$.

These systems can be considered as representatives of van der Waals molecules bound by electrostatic and induction, electrostatic, induction, and dispersion, and pure dispersion forces. In all cases we considered the structures corresponding to the global minima on the corresponding potential energy surfaces.

Except for the He atom, we used the medium-polarized basis sets of Sadlej [10]. For helium we used the [7s3p2d] basis from Ref. [11].

Results

Table 1: Comparison of the induction energy calculated by the second order Møller-Plesset and various nonperturbative methods (all entries are in cm^{-1}).

	$(\text{H}_2\text{O})_2$	$(\text{HF})_2$	$(\text{CO})_2$	$(\text{N}_2)_2$	$\text{He-H}_2\text{O}$
$E_{\text{ind,resp}}^{(20)}$	-666.35	-833.09	-42.87	-15.75	-7.88
$E_{\text{ind,resp}}^{(22)}$	-148.16	-206.41	-16.74	-7.26	-0.50
$\Delta_{\text{ind}}^{(2)}(\text{CCSD, nonr})$	46.94	55.43	8.20	0.48	0.40
$\Delta_{\text{ind}}^{(2)}(\text{CCSD})$	47.49	55.19	7.81	0.49	0.37
$\Delta_{\text{ind}}^{(2)}(\text{QCISD})$	36.17	34.52	6.97	0.17	0.36
$t E_{\text{ind}}^{(22)}$	-116.11	-174.51	-1.78	-4.32	-0.04

Table 2: Components of the interaction energy (in cm^{-1}) calculated for various complexes.

	$(\text{H}_2\text{O})_2$	$(\text{HF})_2$	$(\text{CO})_2$	$(\text{N}_2)_2$	$\text{He-H}_2\text{O}$
$E_{\text{elst}}^{(1)}(4)$	-2202.29	-2094.32	-136.73	-69.22	-7.52
$E_{\text{elst}}^{(1)}(\text{CC})$	-2199.53	-2090.55	-136.81	-69.16	-7.44
$E_{\text{exch}}^{(1)}$	1927.06	2055.02	225.29	116.95	43.12
$E_{\text{ind}}^{(2)}$	-814.51	-1039.50	-59.61	-23.01	-8.38
$E_{\text{exch-ind}}^{(2)*}$	404.81	490.48	46.94	20.42	1.89
$E_{\text{ind}}^{(2)}(\text{CCSD})$	-767.02	-984.31	-51.80	-22.52	-8.01
$E_{\text{exch-ind}}^{(2)}(\text{CCSD})^*$	381.20	464.44	42.75	19.98	1.81
$E_{\text{disp}}^{(2)}$	-703.08	-600.19	-201.45	-143.76	-53.18
$E_{\text{exch-disp}}^{(2)}$	93.71	70.82	11.75	6.64	1.52
$E_{\text{exch-def}}^{(2)}$	-198.00	-207.86	-17.27	-5.14	-2.59
$E_{\text{int}}^{\text{SAPT}}(2)^a$	-1492.30	-1325.56	-128.82	-97.12	-25.14
$E_{\text{int}}^{\text{SAPT}}(\text{CC})^b$	-1465.66	-1292.64	-127.54	-97.01	-24.77
$E_{\text{int}}^{\text{CCSD}}(\text{T})$	-1480.89	-1349.86	-85.95	-87.90	-24.68

* Approximated corrections:

$$E_{\text{exch-ind}}^{(2)}(\text{method}) = \frac{E_{\text{exch-ind,resp}}^{(20)} E_{\text{ind}}^{(2)}(\text{method})}{E_{\text{ind,resp}}^{(20)}}. \quad (10)$$

^aThe electrostatic term approximated as $E_{\text{elst}}^{(1)}(\text{MP4}(\text{SDQ}))$ plus the MP4(T) contribution. The induction and exchange-induction terms approximated by $E_{\text{ind}}^{(2)}(2)$ and $E_{\text{exch-ind}}^{(2)}(2)$, respectively.

^bThe electrostatic term approximated as $E_{\text{elst}}^{(1)}(\text{CCSD})$ plus the MP4(T) contribution. The induction and exchange-induction terms approximated by $E_{\text{ind}}^{(2)}(\text{CCSD})$ and $E_{\text{exch-ind}}^{(2)}(\text{CCSD})$, respectively.

Conclusions

- The convergence of the relaxed Møller-Plesset expansion for the induction energy restricted to the second order appears to be satisfactory in most cases.
- The effect of the third and higher-order terms included in CCSD theory is small. A difference between relaxed and nonrelaxed CCSD induction energy is negligible.
- Comparison of the SAPT and CCSD(T) results suggests that a disagreement between these two sets of the results can be caused by higher-order intramonomer correlation corrections to the dispersion energy, and a more elaborate model of these interactions should be devised.

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