# Dispersion Energy from Density-Functional Theory Description of Monomers

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A method is proposed for calculations of dispersion energy at finite intermonomer separations. It uses a generalized Casimir-Polder formula evaluated with dynamic density susceptibilities provided by time-dependent density-functional theory. The method recovers the dispersion energies of He, Ne, and $H_2O$ dimers to within 3% or better. Since the computational effort of the new algorithm scales approximately as the third power of system size, the method is much more efficient than standard wave-function methods capable of predicting the dispersion energy at a similarly high level of accuracy.

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Density functional theory (DFT) has become the most frequently used method in electronic structure calculations. This method fails, however, when used in the supermolecular approach to compute interaction potentials for systems where dispersion is a significant component. Thus, DFT is not appropriate for studies of intermolecular interactions except for the cases of strongly, electrostatically bound systems. This significantly restricts the size of systems that can be investigated by theory since wave-function methods capable of describing dispersion properly are computationally much more demanding than DFT. Numerous papers have been devoted to this problem and the reader is sent to Ref. [1] for a review and a quantitative analysis.

Symmetry-adapted perturbation theory (SAPT) [2] provides both the conceptual framework and the computational techniques for describing intermolecular interactions, including the dispersion energy. However, the computer resources required by SAPT and other methods with high-level treatment of electron correlation—like many-body perturbation theory at the fourth-order level or the coupled-cluster approaches [3]—make applications to monomers with more than about ten atoms not practical at the present time. Williams and Chabalowski [4] have proposed a perturbational approach where the interaction energies are obtained using only the lowest-order, computationally least demanding SAPT expressions, but replacing the Hartree-Fock (HF) orbitals and orbital energies by the Kohn-Sham (KS) counterparts. We will refer to this approach as SAPT(KS). For medium-size monomers, SAPT(KS) is about 3 orders of magnitude faster than the regular SAPT with high-order treatment of electron correlation. However, the accuracy of the SAPT(KS) predictions was found to be disappointing [4] even for the electrostatic energy which is potentially exact in this approach. In a recent Letter, two of us have demonstrated [5] that some deficiencies of SAPT(KS) stem from an incorrect asymptotic behavior of exchange-correlation potentials (see also Ref. [6]). Upon applying an asymptotic correction in monomer DFT calculations, the SAPT(KS) approach was not only able to accurately recover the electrostatic energy, but also the first-order exchange and second-order induction and exchange-induction energies. For example, for $He_2$ the sum of these corrections has been recovered with errors of 2–5% (relative to the nearly exact values from Ref. [7]) for a range of functionals. Dispersion was reproduced less accurately, with errors of 5–17% for the same functionals. For other systems, the deviations of SAPT(KS) dispersion energies from benchmark results are still larger (12–16% for neon, 19–22% for water, and 33–37% for carbon dioxide dimers [8]), too large to enable computations of quantitatively correct potentials.

In the present Letter we propose a new method for computing the dispersion energy that utilizes frequency-dependent density susceptibilities (FDDS's) predicted by time-dependent DFT in an expression which is a generalization of the asymptotic Casimir-Polder formula. This generalization was derived by Longuet-Higgins [9], Dmitriev and Peinel [10], and McWeeny [11] and applied with coupled Hartree-Fock (CHF) FDDS's (polarization propagators) by Jaszunski and McWeeny [12] and by Knowles and Meath [13].

To define the dispersion interaction, we use the following partitioning of the total Hamiltonian: $H = H_A + H_B + V = F + V + W$, where $H_X$ is the Hamiltonian for monomer $X = A$ or $B$, $V$ is the intermolecular interaction operator, $F = F_A + F_B$ is the sum of the Fock operators for monomers $A$ and $B$, and $W = H_A + H_B - F$ is the intramonomer correlation operator. The dispersion energy of the second order in $V$ is then given by

$$E^{(2)}_{\mathrm{disp}} = \sum_{k\neq0}\sum_{l\neq0} \frac{|\langle \Phi_0^A \Phi_0^B | V \Phi_k^A \Phi_l^B \rangle|^2}{E_0^A + E_0^B - E_k^A - E_l^B}, \quad (1)$$

where $\Phi_i^X$ and $E_i^X$ are the exact eigenfunctions and eigenvalues of $H_X$. This expression can be expanded in powers of $W$ as $E^{(2)}_{\mathrm{disp}} = \sum_{j=0}^{\infty} E^{(2j)}_{\mathrm{disp}}$. We will also use notation

$E^{(2)}_{\rm disp}(2) = E^{(20)}_{\rm disp} + E^{(21)}_{\rm disp} + E^{(22)}_{\rm disp}$. The dispersion energy at the $E^{(2)}_{\rm disp}(2)$ level is available in the current version of the SAPT code [14]. For a dimer consisting of identical molecules, the computational cost of this quantity scales roughly as $n_o^3 n_v^4$ where $n_o$ and $n_v$ are, respectively, the numbers of occupied and virtual orbitals in a monomer [15]. The dispersion energy can also be computed with selected intramonomer correlation effects summed up to infinity, see Refs. [16–18].

The exact dispersion energy as defined by Eq. (1) can be represented by the alternative formula [9–11]

$$E^{(2)}_{\rm disp} = -\frac{1}{2\pi}\int_0^\infty \iiiint \alpha_A(\mathbf{r}_1\mathbf{r}_1' \mid iu)\,\alpha_B(\mathbf{r}_2,\mathbf{r}_2' \mid iu) \times \frac{d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_1' d\mathbf{r}_2'}{|\mathbf{r}_1-\mathbf{r}_2||\mathbf{r}_1'-\mathbf{r}_2'|}\,du, \qquad (2)$$

where

$$\alpha_X(\mathbf{r},\mathbf{r}'|\omega) = 2\sum_{m\neq 0}\frac{E^X_m - E^X_0}{(E^X_m - E^X_0)^2 - \omega^2} \times \langle\Phi^X_0|\hat{\rho}(\mathbf{r})|\Phi^X_m\rangle\langle\Phi^X_m|\hat{\rho}(\mathbf{r}')|\Phi^X_0\rangle, \qquad (3)$$

is the FDDS of monomer $X$ computed at frequency $\omega$. The symbol $\hat{\rho}(\mathbf{r})$ stands here for the electronic density operator $\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r}-\mathbf{r}_i)$, the summation extending over all electrons of the considered molecule. For real $\omega$, $\alpha(\mathbf{r},\mathbf{r}' \mid \omega)$ describes the linear change of electronic density at $\mathbf{r}$ under the influence a one-electron perturbation localized at $\mathbf{r}'$ and oscillating with frequency $\omega$. FDDS's are closely related to the dynamic polarizabilities, e.g., $\alpha_{xy}(\omega) = \iint \alpha(\mathbf{r},\mathbf{r}' \mid \omega)xy'd\mathbf{r}d\mathbf{r}'$. It should be stressed that the dispersion energy expressions, Eqs. (1) and (2), account not only for the asymptotic dipole-dipole ($1/R^6$) term but also include the effects of all higher instantaneous multipoles as well as the short-range contributions resulting from the overlap of monomer charge distributions [2,11]. Therefore, these expressions are valid for finite intermolecular distances (including the repulsive part of the potential).

If the wave functions $\Phi^X_0$ in Eq. (3) are replaced by appropriate HF determinants, $\Phi^X_m$ by singly excited HF determinants, and the differences $E^X_m - E^X_0$ by the corresponding excitation energies, one obtains the uncoupled Hartree-Fock (UCHF) FDDSs and the corresponding expression for dispersion energy reduces to $E^{(20)}_{\rm disp}$. With CHF FDDSs, the so-called "random-phase approximation" (RPA) dispersion energy is obtained [17]. An obvious other option is to use FDDS computed using time-dependent DFT. We will use the name coupled KS (CKS) dispersion energy for the quantity obtained in this way.

The FDDS's of the CHF or DFT theory can be expressed in the form

$$\alpha(\mathbf{r},\mathbf{r}'|\omega) = \sum_{ar,a'r'} C_{ar,a'r'}(\omega) \times \phi_a(\mathbf{r})\,\phi_r(\mathbf{r})\,\phi_{a'}(\mathbf{r}')\,\phi_{r'}(\mathbf{r}'), \qquad (4)$$

where $\phi_a(\mathbf{r})$ [$\phi_r(\mathbf{r})$] are occupied (virtual) orbitals. The coefficients $C_{ar,a'r'}(\omega)$ are closely related to those appearing in expressions for CHF or DFT frequency-dependent polarizabilities [19,20]. A computationally convenient formula for these coefficients is

$$C_{ar,a'r'}(\omega) = -\{(\mathbf{H}^{(2)}\mathbf{H}^{(1)} - \omega^2\mathbf{I})^{-1}\mathbf{H}^{(2)}\}_{ar,a'r'}, \qquad (5)$$

where $\mathbf{I}$ is the unit matrix and the matrices $\mathbf{H}^{(1)}$ and $\mathbf{H}^{(2)}$, written explicitly in Ref. [20], are built from orbital energies and two-electron integrals for the CHF case, whereas in the DFT case the matrix elements contain also integrals of the functional derivative of the exchange-correlation potential. We have neglected the terms involving current densities.

If the CHF or DFT FDDSs are substituted in Eq. (2), one obtains the following expression

$$E^{(2)}_{\rm disp} = -\frac{1}{2\pi}\sum_{ar}\sum_{bs}\sum_{a'r'}\sum_{b's'} v^{rs}_{ab}\, v^{r's'}_{a'b'} \times \int_0^\infty C_{ar,a'r'}(iu)C_{bs,b's'}(iu)du, \qquad (6)$$

where $v^{aa'}_{rr'}$ are electron repulsion integrals. The number of arithmetic operations needed to compute this expression scales as $n_{\rm o}^3 n_{\rm v}^3 I$, where $I$ is the number of integration points. This scaling and the need to perform a partial four-index transformation makes such a straightforward approach much more time consuming than the conventional DFT calculations. However, the evaluation of formula (6) can be sped up by orders of magnitude if products of orbitals are replaced by expansions in terms of some one-electron basis. In fact, for a given $\omega$, $\alpha_X(\mathbf{r},\mathbf{r}'|\omega)$ is a function of $\mathbf{r}$ and $\mathbf{r}'$ and can always be written as an expansion into binary products of orbitals

$$\alpha_X(\mathbf{r},\mathbf{r}'|\omega) = \sum_{kl} C^X_{kl}(\omega)\,\chi^X_k(\mathbf{r})\,\chi^X_l(\mathbf{r}'), \qquad (7)$$

where $\chi^X_k(\mathbf{r})$, $k = 1,2,\ldots,n_X$, is some appropriate set of primitive one-electron functions for monomer $X$. Expression (3) then takes the form

$$E^{(2)}_{\rm disp} = -\frac{1}{2\pi}\int_0^\infty \sum_{kl}\sum_{k'l'} C^A_{kl}(iu)\,C^B_{k'l'}(iu)J_{kk'}J_{ll'}du, \qquad (8)$$

where $J_{kk'}$ are the Coulomb integrals

$$J_{kk'} = \iint \frac{\chi^A_k(\mathbf{r})\chi^B_{k'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'. \qquad (9)$$

Evaluation of dispersion energies is now reduced to a multiplication of the $n_X \times n_X$ matrices formed by the coefficients $C^A_{kl}(\omega)$, $C^B_{k'l'}(\omega)$, and the Coulomb integrals $J_{kk'}$. If $n_A > n_B$, the cost of computation scales as $n_A^2 n_B I$. Fitting of products of orbitals has recently been quite broadly used in electronic structure calculations, see, e.g., Ref. [21]. The experience of these papers shows that $n_X$ can be chosen small compared to $n_o n_v$ without any significant reduction of accuracy in the computed quantities. Thus, the cost of computing the CKS dispersion energies scales comparably to standard DFT calculations.

The DFT calculations for monomers were done with CADPAC [22] using the functionals B97-2 [23,24], PBE0 [25,26], and HCTH407 [27,28]. The asymptotic correction (AC) of the Fermi-Amaldi form was applied as prescribed by Tozer and Handy [29]. All results have been converged with respect to quadrature grids used in the DFT calculations and in Eq. (8). In the latter case, $I = 8$ was sufficient. For $He_2$ we have used dimer-centered "plus" form of basis sets (for consistency with Ref. [5]), whereas for the two other systems monomer-centered plus form [30]. All CHF and CKS calculations utilized Cartesian functions, whereas standard SAPT and SAPT(KS) utilized spherical functions except for $He_2$.

The results for $He_2$, $Ne_2$, and $(H_2O)_2$ presented in Tables I, II, and III, respectively, demonstrate the remarkable accuracy that can be achieved by the CKS method with AC. This method recovers benchmark dispersion energies with absolute errors from 0.4 to 3.2% for the range of systems and functionals considered. The performance of the functionals improves in the order: HCTH407, PBE0, B97-2. The asymptotic correction increases the accuracy in all cases, sometimes by an order of magnitude, except for the water dimer. In all cases the CKS/AC method performs significantly better than SAPT(KS)/AC: for $Ne_2$ and $(H_2O)_2$ by about an order of magnitude.

TABLE I. SAPT, SAPT(KS), CHF, and CKS dispersion energies (in kelvins) for $He_2$ computed at $R = 5.6$ bohrs using the basis Dc147 of Ref. [7]. The benchmark results, obtained by SAPT employing various orbital and geminal basis sets [7], are expected to be accurate to 0.01 K.[a,b,c]

| | | SAPT(KS) | | CKS | |
|---|---|---|---|---|---|
| Method | SAPT | no AC | AC | no AC | AC |
| Bchmrk $E^{(20)}_{\mathrm{disp}}$ | −17.17 | | | | |
| Bchmrk $E^{(2)}_{\mathrm{disp}}$ | −22.39 | | | | |
| $E^{(20)}_{\mathrm{disp}}$ | −17.07 | | | | |
| $E^{(2)}_{\mathrm{disp}}(2)$ | −21.36 ( − 4.6) | | | | |
| CHF | −20.93 (6.5) | | | | |
| HCTH407 | | −30.77[d] | −25.79[d] | −27.65 | −23.05 |
| | | (37.4) | (15.2) | (23.5) | (2.9) |
| B97-2 | | −25.50 | −23.05 | −25.13 | −22.62 |
| | | (13.9) | (2.9) | (12.2) | (1.0) |
| PBE0 | | −25.89 | −23.36 | −25.55 | −22.94 |
| | | (15.6) | (4.3) | (14.1) | (2.5) |

[a] The DFT results are for "very high" grid numerical integration [22]. "High" and "extreme" options give negligible differences.
[b] Splicing constants $c_1 = 3.0$ and $c_2 = 4.0$ in AC.
[c] Percentage errors (in parentheses) are relative to benchmark $E^{(2)}_{\mathrm{disp}}$.
[d] Reference [5].

The performance of the CKS method can be contrasted with the performance of the standard SAPT in the same basis set. This comparison is fully meaningful only for $He_2$ and in this case the respective errors are 1.0–2.9% vs 4.6%. For $Ne_2$ and $(H_2O)_2$, the benchmark and the standard SAPT results are close to each other as these differ only by the basis set size. Judging from $He_2$ results, one cannot exclude that the CKS results are closer to exact dispersion energies than the standard SAPT results. This may explain why for water the application of AC apparently does not improve accuracy for some functionals. However, the role of AC is small for $(H_2O)_2$ due to the relatively short intramonomer distance.

The highly accurate dispersion energies computed using the CKS/AC method confirm the significant predictability of recently developed density functionals. One could have anticipated the results obtained by us based on published CKS calculations (see, e.g., Ref. [32]) of static polarizabilities which often can reproduce known accurate values to a better accuracy than high-level coupled-cluster methods. Assessment of accuracy is more difficult for dynamic polarizabilities, nevertheless CKS results from Ref. [33] appear to be rather accurate. As discussed earlier, these quantities are closely related to FDDS functions determining the dispersion energy.

In summary, we have shown that highly accurate dispersion energies can be computed from asymptotically corrected DFT FDDS at a cost comparable to regular DFT calculations. This high accuracy observed here for equilibrium configurations holds for the whole range of intermolecular separations (to be published). The method therefore provides the currently most accurate approach for practical calculations of dispersion interactions for

TABLE II. SAPT, SAPT(KS), CHF, and CKS dispersion energies (in $cm^{-1}$) for $Ne_2$ at $R = 3.1$ Å. The basis set used for the benchmark calculations was aug-cc-pV5Z [31] plus a set of $[3s2p1d1f]$ bond functions from Ref. [7]. All other calculations used a smaller, daug-cc-pVTZ set with the same bond functions.[a,b,c]

| | | SAPT(KS) | | CKS | |
|---|---|---|---|---|---|
| Method | SAPT | no AC | AC | no AC | AC |
| Bchmrk $E^{(20)}_{\mathrm{disp}}$ | −46.46 | | | | |
| Bchmrk $E^{(2)}_{\mathrm{disp}}(2)$ | −58.32 | | | | |
| $E^{(20)}_{\mathrm{disp}}$ | −46.30 | | | | |
| $E^{(2)}_{\mathrm{disp}}(2)$ | −59.04 (1.2) | | | | |
| CHF | −50.10 (14.1) | | | | |
| HCTH407 | | −83.18 | −73.37 | −68.65 | −60.18 |
| | | (42.6) | (25.8) | (17.7) | (3.2) |
| B97-2 | | −70.16 | −65.47 | −62.97 | −58.53 |
| | | (20.3) | (12.3) | (8.0) | (0.4) |
| PBE0 | | −71.12 | −66.67 | −63.83 | −59.60 |
| | | (21.9) | (14.3) | (9.4) | (2.2) |

[a] See footnote *a* in Table I.
[b] See footnote *b* in Table I.
[c] Percentage errors (in parentheses) are relative to benchmark $E^{(2)}_{\mathrm{disp}}(2)$.

TABLE III. SAPT, SAPT(KS), CHF, and CKS dispersion energies (in kcal/mol) for water dimer at a near equilibrium configuration (monomers in vibrationally averaged geometry, dimer in $C_s$ symmetry, center of mass distance of 3 Å, nonlinearity of hydrogen bond of 8.5°, and the angle of the acceptor bisector with the vector joining centers of mass of 129.3°). The basis set used for benchmarks was aug-cc-pVQZ [31], whereas for all calculations it was aug-cc-pVTZ plus (in both cases) a set of $[3s2p1d]$ bond functions from Ref. [30][a,b,c].

| | | SAPT(KS) | | CKS | |
|---|---|---|---|---|---|
| Method | SAPT | no AC | AC | no AC | AC |
| Bchmrk $E_{\mathrm{disp}}^{(20)}$ | −2.131 | | | | |
| Bchmrk $E_{\mathrm{disp}}^{(2)}(2)$ | −2.472 | | | | |
| $E_{\mathrm{disp}}^{(20)}$ | −2.111 | | | | |
| $E_{\mathrm{disp}}^{(2)}(2)$ | −2.472 (0.0) | | | | |
| CHF | −2.184 ( − 11.7) | | | | |
| HCTH407 | | −3.718 | −3.448 | −2.608 | −2.433 |
| | | (50.4) | (39.5) | (5.5) | ( − 1.6) |
| B97-2 | | −3.125 | −3.032 | −2.484 | −2.414 |
| | | (26.4) | (22.7) | (0.5) | ( − 2.3) |
| PBE0 | | −3.112 | −3.028 | −2.480 | −2.417 |
| | | (25.9) | (22.5) | (0.3) | ( − 2.2) |

[a] See footnote *a* in Table I.
[b] See footnote *b* in Table I.
[c] Percentage errors (in parentheses) are relative to benchmark $E_{\mathrm{disp}}^{(2)}(2)$.

large monomers, possibly containing as many as 20 atoms. This will bring important biophysical applications within reach (e.g., interactions involving DNA bases, small polypeptides, and sugars). When the present work was nearly completed, a paper by Hesselmann and Jansen [34] appeared that presented results of calculations with a somewhat similar approach.

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