Computational Consequences of Neglected First-Order van der Waals Forces

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We have computed the widely neglected first-order interaction between neutral atoms. At interatomic separations typical of condensed media, it is nearly equal to the $-1/r^6$ second-order London energy inferred from interactions in gases. Our results, without the exchange forces that lead to covalent bonding, suggest that the quality of non-bonding attraction between neutral atoms of molecules in condensed media differs from the $-1/r^6$ form usually ascribed to it. If we add first-order and all second-order terms, we obtain energies nearly five times the $-1/r^6$ London energies which dominate only at the atomic separations found in gases. For computation, we propose a practical, accurate form of energy to replace the qualitatively inaccurate Lennard-Jones and harmonic forms casually assumed to hold at the interatomic separations found in condensed media.

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Does the van der Waals potential energy between two neutral atoms fall off as $-1/r^6$ at separations of a few Å? Is the widely neglected first-order van der Waals potential zero at the interaction distances within condensed media? Should one use a Lennard-Jones 6-12 potential in computer simulations? Because it is no longer necessary to sacrifice accuracy for computational convenience, we numerically re-examine these old questions, find that common practice leads to qualitative error, and propose an accurate but practical alternative to the mathematically convenient but potentially misleading Lennard-Jones (L-J) and harmonic forms.

Motivated by an intriguing footnote in Landau and Lifshitz [1], we compute the first-order van der Waals potential for two hydrogen atoms, without the exchange interaction that creates covalent bonds. It is nearly equal to the $1/r^6$ second-order London energy found from the same wave functions when evaluated over a range of separations where both exceed $kT$ at room temperature. We then compute the potential energy to second-order, obtaining an expression that reassuringly reproduces the expected dominance of the $1/r^6$ London term as $r \to \infty$. The net result at separations $3a_0 < r < 5a_0$ (Bohr radius $a_0$) is an energy 4 to 5 times that expected from a London interaction, which emerges to dominate only in the $r > 10a_0$ limit.

We next examine the additivity of the interactions of several particles, usually taken to be additive in first and second order; the Axilrod-Teller-Muto force [2] is a third-order effect. In fact, energies add in first-order perturbation theory but not in second order unless one neglects first-order terms.

 Constructed to fit the measured equilibrium separation $r_s$ and the measured condensation energy energy $V(r_s)$ as well as to have the large-$r$ asymptotic form $1/r^6$, the Lennard-Jones potential is too hard for $r < r_s$ and varies incorrectly for $r > r_s$. Harmonic potentials work only near energy minima. We propose a simple, phenomenological potential that can fit spectroscopic data and that behaves appropriately at all distances.

For our calculations, we take the hamiltonian for two interacting hydrogen atoms to be $H = H_0 + W$ in which $H_0$ is a sum of two isolated-hydrogen-atom hamiltonians and the perturbation $W$ is a function of the distance $r$ between the two protons

$$W = \frac{e^2}{r} + \frac{e^2}{|\vec{r} + \vec{r}_2 - \vec{r}_1|} - \frac{e^2}{|\vec{r} + \vec{r}_2|} - \frac{e^2}{|\vec{r} - \vec{r}_1|}$$

(1)

Here $r = |\vec{r}|$ and $e$ is the charge of the electron in units with $\alpha = e^2/(\hbar c) \approx 1/137$. The first-order correction to the energy is $\Delta E_1(r) = \langle 0|W|0 \rangle$ in which the unperturbed ground state $|0\rangle = |100,100\rangle$ is two $1s$ states separated by a distance $r$. Its wave function is $|\vec{r}_1,\vec{r}_2,0\rangle = (1/\sqrt{\alpha a_0^3}) \exp(-r_1/\alpha a_0 - r_2/\alpha a_0)$ where $a_0 = \hbar^2/(mc^2)$ is the Bohr radius, $r_1 = |\vec{r}_1|$, and $r_2 = |\vec{r}_2|$. Integration of $\langle 0|W|0 \rangle$ yields

$$\Delta E_1(r) = m c^2 \alpha^2 e^{-2r/a_0} \left( \frac{a_0}{r} + \frac{5}{8} - \frac{3r}{4a_0} - \frac{r^2}{6a_0^2} \right).$$

(2)

London and others [4] applied second-order perturbation theory to the potential [1], expanded for large $r$, and got $\Delta E_L(r) = -6.50 m c^2 \alpha^2 e_0^6/a_0^6$. Fig. 1 shows that the two energies $\Delta E_1(r)$ and $\Delta E_L(r)$ are nearly equal for $3a_0 < r < 5a_0$, where both are reliable and greater than $kT = 1/40$ eV. Because $\Delta E_1(r)$ is the first-order result, and $\Delta E_L(r)$ is an approximation to second-order perturbation theory, the two can be added. That is, to (approximate) second order in the perturbation $W$ and within the London approximation, the van der Waals energy is $\Delta E_1(r) + \Delta E_L(r)$, different by about...
100% from the London-only result for $3a_0 < r < 5a_0$. Because $\Delta E_1(r)$ decreases with $r$ as $\exp(-2r/a_0)$, the London potential $\Delta E_L(r)$ dominates at large $r$. But it is not until $r = 5.78a_0$ that $|\Delta E_L(r)| > 2|\Delta E_1(r)|$. By then $|\Delta E_L(r)| < kT/5$.

What about second order beyond $\Delta E_L(r)$? The correction to the ground-state energy due to the perturbation $W$ is

$$\Delta E_2(r) = - \sum_{n \neq 0} \frac{|\langle 0|W|n \rangle|^2}{E_n - E_0} \quad (3)$$

in which the sum is over all eigenstates $|n\rangle$ of the Hamiltonian $H_0$ except $|0\rangle$. If the first state to contribute to the sum has energy $E_1$, then $0 < E_1 - E_0 \leq E_n - E_0$ or $-1/(E_1 - E_0) \leq -1/(E_n - E_0)$. So the second-order change in the energy is bounded by

$$- \frac{1}{E_1 - E_0} \sum_{n \neq 0} |\langle 0|W|n \rangle|^2 \leq \Delta E_2(r) \leq 0. \quad (4)$$

The first states to contribute to the sum are those in which one of the electrons is in the $n = 2$ level, so $E_1 = -(1/2)\alpha^2 m c^2(1 + 1/4)$. But because the hydrogen wave functions fall off as $\exp(-r/(n a_0))$, at long distances the first states to contribute are those with both electrons in the $n = 2$ level; they have $E_1 = -(1/2)\alpha^2 m c^2(1 + 1/4 + 1/4)$. Without the energy denominators, the sum over intermediate states follows from completeness:

$$\sum_{n \neq 0} |\langle 0|W|n \rangle|^2 = \langle 0|W^2|0 \rangle - \langle 0|W|0 \rangle^2, \quad (5)$$

where $\langle 0|W|0 \rangle$ is the first-order result $\Delta E_1(r)$, Eq. (2).

Evaluating the mean value of $W^2$ involves the integral

$$G(x) = (2/\pi) \int_0^\infty dy \left(y^2 / (1 + y^2) \exp(-2y^2)\right)$$

a function only of the length $x = |\vec{x}| = |\vec{r}|/a_0$. We find

$$G(x) = \frac{1}{x} \left[ (1 + 2x) e^{-2x} E_1(2x) + (1 - 2x) e^{2x} E_1(2x) \right] \quad (6)$$

in which $E_1$ and $E_1$ are exponential integrals. $G(x)$ contributes to the integral $J(x)$

$$J(x) = \frac{1}{4x} \int_0^\infty y G(y) \left( (1 + 2|x - y|) e^{-2|x - y|} - (1 + 2x + y) e^{-2x+y} \right) dy \quad (7)$$

that represents the square of the interaction of the two electrons. The product of electron-electron and electron-proton energies is described by the function $K(x)$

$$K(x) = \left\{ 4 \ln 2 - 3 + \frac{2 \ln 2}{x} + 2x \right. \nonumber$$

$$- \left( 4 + \frac{2}{x} \right) [E_1(2x) - \gamma - \ln(2x)] e^{-2x} \nonumber$$

$$+ \left( 4 - \frac{2}{x} \right) e^{2x} [E_1(2x) - E_1(4x)] \quad (8)$$

FIG. 1: The first-order van der Waals energy $\Delta E_1(r)$, Eq. (2), (solid, red) is nearly equal to the London result $\Delta E_L(r)$ (long dashes, green) when both are reliable and greater than $kT$ (dotted, plum). The change in the sum $\Delta E(r) = \Delta E_1(r) + $ $\Delta E_2(r)$ (dashes, blue) as given by second-order perturbation theory, $\eqref{9}$, is 4 to 5 times greater than the London term for $3a_0 < r < 5a_0$. The potential of $\eqref{15}$ with $a = 336$ eV, $b = 1.97a_0^{-1}$, $c = 0.47a_0^{-1}$, $d = 397a_0^{-2}$ eV, and $e = 14093a_0^{-2}$ (dashes, light blue) overlaps $\Delta E(r)$.

in which $\gamma = 0.5772\ldots$ is the Euler-Mascheroni constant. In terms of $\Delta E_1$, $J$, and $K$, the second-order correction $\Delta E_2(r)$ to the energy at $r = a_0 x$ becomes $-(f a_0/e^2) (\langle 0|W^2|0 \rangle - \langle 0|W|0 \rangle^2)$ or

$$\Delta E_2(r) = -f a_0 \frac{e^2}{e^2} \left\{ - \left( \Delta E_1(r) - \frac{\gamma^2}{r} \right)^2 \right. \nonumber$$

$$+ \frac{2e^4}{r^2} \left[ 1 - (1 + x) e^{-2x} \right]^2 \quad (9)$$

$$+ \frac{e^4}{a_0^2} [G(x) + J(x) + K(x)] \right\}.$$
Now the perturbation $W$ is $W = W_{12} + W_{23} + W_{13}$ in which the pair potential $W_{ij}$ is
\[
W_{ij} = \frac{e^2}{|\mathbf{R}_j - \mathbf{R}_i|} + \frac{e^2}{|\mathbf{R}_j + \mathbf{r}_j - \mathbf{R}_i - \mathbf{r}_i|} - \frac{e^2}{|\mathbf{R}_j + \mathbf{r}_j - \mathbf{R}_i - \mathbf{r}_i|} - \frac{e^2}{|\mathbf{R}_j - \mathbf{R}_i - \mathbf{r}_i|}.
\]
(11)

To first order in the perturbation $W$, the change in the energy $\Delta E_1 = \langle 1, 2, 3 | W_{12} + W_{23} + W_{13} | 1, 2, 3 \rangle$ is additive: $\Delta E_1 = \langle 1, 2 | W_{12} | 1, 2 \rangle + \langle 2, 3 | W_{23} | 2, 3 \rangle + \langle 1, 3 | W_{13} | 1, 3 \rangle$.

But at smaller separations the cross-terms do not vanish. To second order in $W$, $\Delta E_2$ is not quite additive. The mean value of $W_{12} W_{23}$, e.g., involves a non-zero sum over the intermediate states $|1, 2, 3, 3, 0\rangle$, $|1, 2, 3, 3, 0\rangle$.

\[
\langle 1, 2, 3 | W_{12} W_{23} | 1, 2, 3 \rangle = \sum_n \langle 1, 2, 3 | W_{12} | 1, 2 \rangle \langle 2, 3 | W_{23} | 1, 2 \rangle + \langle 1, 2, 3 | W_{12} W_{23} | 1, 2, 3 \rangle - \langle 1, 2, 3 | W_{12} | 1, 2 \rangle \langle 2, 3 | W_{23} | 1, 2 \rangle - \langle 1, 2, 3 | W_{12} W_{23} | 1, 2, 3 \rangle \neq 0.
\]
(12)

Failure of additivity already occurs at second order.

In the usual treatment, one expands the perturbation $W$ in powers of $1/r$ keeping only terms as big as $1/r^6$ at large $r$ and neglects terms like Eq. (12). If $\mathbf{R}_2 - \mathbf{R}_1$ points in the 3-direction, then the leading term in the matrix element $\langle 1, 2 | W_{12} | 1, 2 \rangle$ involves $(x_1 x_2 + y_1 y_2 - 2z_1 z_2)/|\mathbf{R}_2 - \mathbf{R}_1|^3$ which vanishes because of the spherical symmetry of the ground state of atom 1. This neglect of the first-order van der Waals force defers non-additivity to the third order of perturbation theory in the Axilrod-Teller-Muto formulation [2,3]. This deferral, however, is probably inconsequential compared with the prior omission of purely additive first-order interactions.

CLeary there is room for improvement on the Lennard-Jones [8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23] and harmonic forms
\[
V_{LJ}(r) = |V(r_s)| \left[ \left( \frac{r_s}{r} \right)^{12} - 2 \left( \frac{r_s}{r} \right)^6 \right],
\]
(13)
\[
V_H(r) = V(r_s) + \frac{(r - r_s)^2}{2} \frac{d^2V(r_s)}{dr^2}.
\]
(14)

What to do? We suggest using the form
\[
V(r) = ae^{-br}(1 - cr) - \frac{d}{r^6} + e^{-6r}.
\]
(15)

The terms involving $a$, $b$, and $c$ appear in Eq. (2) for $\Delta E_1(r)$, were proposed by Rydberg [24] to incorporate spectroscopic data, but were largely ignored until recently [25,26]. The constant $d = C_6$ is the coefficient of the London tail. The new term $e^{-6r}$ cures the London singularity; as $r \to 0$, $d/r^6 + e^{-6r} \to dr^6/e$ and $V(r) \to a$, finite. But as $r \to \infty$, $V(r)$ approaches the London term, $V(r) \to -d/r^6 = -C_6/r^6$.

![FIG. 2: The phenomenological potential \( V(r) \) with \( a = 53.8 \) eV, \( b = 2.99 \) Å\(^{-1} \), \( c = 2.453 \) Å\(^{-1} \), \( d = C_6 = 3.884 \) eV Å\(^6 \), and \( e = 47.6 \) Å\(^2 \) (solid, red) is finite, fits the RKR spectral points for molecular hydrogen (crosses, blue), and gives the correct London tail for \( r > 3 \) Å. The harmonic potential \( V_H \) (dashes, green) is accurate only near its minimum.](image)

To test the ability of the potential \( V(r) \) to represent covalent bonds, we used Gnuplot [27] to choose \( a, b, c, d, \) and \( e \) so as to fit Eq. (15) to the experimental potentials of molecular \( H_2, N_2, \) and \( O_2 \) obtained from spectroscopic data [28,29,30] by the Rydberg [22,24]-Klein [31]-Rees [32] (RKR) method. For \( H_2 \), we set \( d \) equal to the London value, \( d = C_6 = 6.5 \) mc\(^2\) \( \alpha^2 \) Å\(^6\). Fig. (2) shows that the potential of Eq. (15) (solid, red) goes through the RKR points for \( H_2 \) (crosses, blue), while the harmonic potential (14) (dashed, green) is accurate only near its minimum and is dreadful for \( r > r_s \). The fits of $V(r)$ to the \( N_2 \) and \( O_2 \) RKR points were equally good. The potential $V(r)$ of Eq. (15) represents covalent bonds better than the harmonic potential $V_H$ of Eq. (11) (or $V_{LJ}$).

Can $V(r)$ represent weak noncovalent bonds? Using Gnuplot, we fitted $a, b, c, d, \) and $e$ in Eq. (15) to calculated He$_2$ [33] or empirical Ar$_2$ and Kr$_2$ [34] potentials, setting $d$ equal to the respective London coefficient. Fig. (3) shows that $V(r)$ of Eq. (15) (solid, red) fits the empirical points [34] for Kr$_2$ (crosses, blue), but that the Lennard-Jones potential $V_{LJ}$ of Eq. (13) (dashes, green) is too low for $r > 4$ Å. Fig. (4) shows that $V(r)$ fits the empirical Kr$_2$ points, but that $V_{LJ}$ is much too hard for $r < 4$ Å. The fits for He$_2$ and Ar$_2$ were equally good. Figs. (2-4) would look even better with the London $d$ treated as a free parameter. The potential $V(r)$ of Eq. (15) represents weak noncovalent bonds better than $V_{LJ}$ or $V_H$. $V_{LJ}$ is unrealistically hard for $r < r_s$; it can wrongly reject Monte Carlo moves that put atoms slightly too close, frustrating M-C searches for the native states of macromolecules.
FIG. 3: The potential $V$ of Kr-Kr attraction (Eq. (15) with $a = 2296$ eV, $b = 2.5136$ Å$^{-1}$, $c = 0.2467$ Å$^{-1}$, $d = 78.2146$ eV Å$^6$, and $e = 407923$ Å$^{12}$) (solid, red) is finite, fits the Kr$_2$ Aziz points (crosses, blue), and gives the correct London tail. When matched at the minimum, the Lennard-Jones form $V_{LJ}$ (Eq. (13) as in Fig. (3)) (dashes, green) is too low for $r > 4$ Å.

FIG. 4: Positive potential $V$ (Eq. (15) as in Fig. (3)), Kr$_2$ Aziz points (crosses, blue), L-J form $V_{LJ}$ (Eq. (13) as in Fig. (3)).

The van der Waals potential is often as large in first order as in second. The potential (15) may be useful in macromolecular simulations that involve not only bonded but also non-bonded atoms. Given the differences between Eq. (15) and the popular Lennard-Jones form, it would be worthwhile to examine the consequences of these differences in numerical simulations.

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