Evaluation of Long-Range Retarded Interaction Energies

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The most important contributions to the expansion of the exact long-range retarded interaction energy, between two nondegenerate atoms, are evaluated accurately for the H–H, H–He, and He–He interactions.

I. INTRODUCTION

Recently, Meath and Hirschfelder1 have obtained expressions for the $1/R$ expansion of the retarded (or relativistic) long-range interaction energy between two nondegenerate molecules separated by a distance $R$. Their coefficient labeled $W_4$ in Paper I is the most significant term in the expansion.2 It is the coefficient of the energy term depending on the inverse fourth power of the intermolecular separation and is of the order $a^2$ smaller than $C_4$, the van der Waals coefficient, where $a$ is the fine-structure constant.

In this paper we perform an accurate evaluation of $V_4$ for the H–H, H–He, and He–He interactions. We show how $W_4$ can be obtained from a minimal principle and use the method of Karpplus and Kolker3 for evaluating it. The numerical results are contained in Sec. III. In the Appendix other coefficients are considered including the van der Waals coefficient and thereby we have a check on recent calculations.4–6

II. REDUCTION OF $W_4$

The coefficient $W_4$ [see Eq. (48) of Ref. 1] is given by

$$W_4 = \frac{1}{2} \sum_j \sum_k \left[ f^{(4)}(j) f^{(2)}(k) / (\Delta a_a(j) + \Delta a_b(k)) \right],$$

where $a$ and $b$ designate the separated atoms and where

$$\Delta a_a(j) = E_a(j) - E_a(0),$$

$f^{(4)}(j)$ being the energy of the $j$th level in the isolated atom $a$, and where $f^{(2)}(j)$ is the oscillator strength defined in the usual way:

$$f^{(2)}(j) = 2 \Delta a_a(j) |\langle 0 | Z | j \rangle_a|^2,$$

with

$$Z_a = \sum_{i=1}^{N_a} Z_{ai},$$

$N_a$ being the number of electrons on center $a$, and $Z_{ai}$ is the $Z$ coordinate of the $i$th electron measured from center $a$. Using the identity

$$2 \Delta a_a \Delta a_b = (\Delta a_a + \Delta a_b)^2 - (\Delta a_a^2 + \Delta a_b^2),$$

Eq. (1) separates into two parts. That is, on substitution of Eqs. (2) and (3) into (1) we can write

$$W_4 = (1 + \sigma_{ab}) [1] + [2],$$

where

$$[1] = \sum_j \sum_k \Delta a_a(j) |\langle 0 | Z | j \rangle_a|^2 |\langle 0 | Z | k \rangle_b|^2,$$

$$[2] = - \sum_j \sum_k \left[ \Delta a_a(j)/\Delta a_b(k) \right]^2 \times \langle 0 | Z | j \rangle_a^2 |\langle 0 | Z | k \rangle_b|^2,$$

and where $\sigma_{ab}$ is the permutation operator on the subscripts $a$ and $b$. The expression for $[1]$ simplifies immediately, for the sums over the states of the two atoms can be separated. We write

$$[1] = \frac{1}{2} \sum_j S_a(j) S_b(j),$$

where

$$S_a(j) = \sum_j \left[ \Delta a_a(j) / \Delta a_b(k) \right]^2 f^{(2)}(j).$$

Applying the sum rules4 Eq. (5) becomes

$$[1] = \frac{1}{2} \sum_j S_a(j) |\langle 0 | Z^2 | 0 \rangle_b|^2,$$

and therefore $[1]$ can be evaluated knowing only the ground-state wavefunction of the separated atoms.

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2. The validity of these expansions has been discussed by many authors; see references in Paper II. In all cases $R$ must be sufficiently large that the charge distributions of the interacting molecules do not overlap appreciably.


TABLE I. Comparison of the results of this paper for $\tilde{W}_i$ with
the Umöd approximation described in Ref. 1. In the case of H,
the average energy obtained from Eq. (66) of Ref. 1 is 0.489.

<table>
<thead>
<tr>
<th></th>
<th>H-H</th>
<th>H-He</th>
<th>He-He</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{W}_i$a</td>
<td>0.4628065</td>
<td>0.503070</td>
<td>0.66428</td>
</tr>
<tr>
<td>Unsöldb</td>
<td>0.513</td>
<td>0.568</td>
<td>0.786</td>
</tr>
</tbody>
</table>

a Reference 11.
b Reference 2.

We now make use of the identity connecting coordinate and momentum matrix elements,

$$\langle j | P_Z | 0 \rangle_a = i \Delta \theta_a (j) \langle j | Z | 0 \rangle_a, \tag{8}$$

where

$$\langle P_Z \rangle_a \equiv \sum_{i=1}^{N} \rho_{i}^{a} P_{Z_{i}}$$

if $Z_0$ is defined as above. Using this in [2] we obtain

$$[2] = -\sum_{j \neq k} \frac{\langle 0 | P_Z | \bar{j} \rangle_a \langle 0 | Z | \bar{k} \rangle_a}{\Delta \theta_a (j) + \Delta \theta_a (k)}, \tag{9}$$

The resulting expression for [2] can now be seen to be in the form of a second-order energy of the combined
Hamiltonian

$$H_0(a, b) = H_0(a) + H_0(b),$$

under the perturbation

$$\Gamma_{a,b} = P_{Z} Z_{b},$$

where $H_0(a) + H_0(b)$ are the Hamiltonians of the separated atoms. Consequently [2] can be evaluated by
a minimal principle knowing only the ground-state wavefunctions of the separated atoms. That is, we can,
in the usual manner, minimize the expression

$$E^{(2)}(P_Z, Z_0) = \langle \bar{j} | H_0(a) + H_0(b) - E_a(0) - E_b(0) | \bar{0} \rangle + 2 \langle \bar{j} | P_Z Z_0 | \bar{0} \rangle, \tag{10}$$

where

$$| 0 \rangle = | 0 \rangle_a = | 0 \rangle_b,$$

and

$$E^{(2)}(P_Z, Z_0)$$

to find an optimal $E^{(2)}(P_Z, Z_0)$ which will then be an upper bound to [2] in Eq. (9). In this way one can
obtain a fundamental upper bound on $\tilde{W}_i$ itself; that is, we can write

$$\tilde{W}_i = \langle 1 + \theta_a \rangle \left[ \frac{1}{2} \lambda \langle 0 | Z | 0 \rangle_b + E^{(2)}(P_Z, Z_0) \right], \tag{11}$$

where

$$\tilde{W}_i \geq \tilde{W}_i.$$  

III. EVALUATION OF $\tilde{W}_i$

To evaluate $E^{(2)}(P_Z, Z_0)$ we observe, following Kaplis and Kolker, that if in Eq. (10) we set

$$| \bar{j} \rangle = \sum_j \sum_k C_{j,k} | j \rangle_a | \bar{k} \rangle_b,$$

where the orthogonalized basis sets $| j \rangle_a$ and $| \bar{k} \rangle_b$ diagonalize $H_0(a)$ and $H_0(b)$, respectively, then the
optimal $E^{(2)}(P_Z, Z_0)$ can be written in a form like that of Eq. (9), namely

$$E^{(2)}(P_Z, Z_0) = -\sum_{j=1}^{N} \sum_{k=1}^{M} \frac{\langle 0 | P_Z | j \rangle_a \langle 0 | Z | k \rangle_b}{\Delta \theta_a (j) + \Delta \theta_a (k)}, \tag{13}$$

where $\Delta \theta_a (j)$ and $\Delta \theta_a (k)$ are the eigenvalues of the above eigenvectors, $N$ and $M$ being the number of
vectors included in the basis sets.

As the coefficients in Ref. 1 involve, in general, matrix elements of spherical tensors, the general form
chosen for basis vectors is

$$\psi_{\ell_{\lambda}}(a) = F_{\ell_{\lambda}}(a) \phi_{\ell_{\lambda}}^{(a)}, \tag{14}$$

where

$$F_{\ell_{\lambda}}(a) = \sum_{l=1}^{N} r_{l}^{a} Y_{\ell_{\lambda}}^{(l)}(a), \quad s \geq l,$$

the $Y_{\ell_{\lambda}}^{(l)}$ being the spherical harmonics. This set must now be made simultaneously orthogonal and diagonal
with respect to $H_0(a)$ to obtain the approximate eigenvectors of Eq. (12). Further, since these functions have
the property that Eq. (8) will be satisfied by the approximate eigenvalues and eigenvectors, i.e.,

$$\langle j | P_Z | 0 \rangle = i \Delta \theta_a (j) \langle j | Z | 0 \rangle_a, \tag{15}$$

it follows that one need only evaluate the dipole matrix elements to obtain $E^{(2)}(P_Z, Z_0)$ and the corresponding
expression with $a$ and $b$ interchanged. Thus, for the calculation of $\tilde{W}_i$ we need only keep the vectors $\psi_{\ell_{\lambda}}$
of Eq. (14), whereas in the evaluation of the coefficient

TABLE II. Values of effective oscillator strengths and eigenenergies
for H and He in atomic units.*

<table>
<thead>
<tr>
<th>$\ell_{\lambda}$</th>
<th>$J_{\ell_{\lambda}}$</th>
<th>$\Delta \ell_{\lambda}$</th>
<th>$J_{\ell_{\lambda}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.448619993</td>
<td>0.37500006</td>
<td>0.27055077</td>
</tr>
<tr>
<td>2</td>
<td>0.08803654</td>
<td>0.4553064</td>
<td>0.3481857</td>
</tr>
<tr>
<td>3</td>
<td>0.00933244</td>
<td>0.4867761</td>
<td>0.4935984</td>
</tr>
<tr>
<td>4</td>
<td>0.10723836</td>
<td>0.5613416</td>
<td>0.982775</td>
</tr>
<tr>
<td>5</td>
<td>0.10897586</td>
<td>0.6836018</td>
<td>0.3027825</td>
</tr>
<tr>
<td>6</td>
<td>0.08703299</td>
<td>0.8916902</td>
<td>0.0646603</td>
</tr>
<tr>
<td>7</td>
<td>0.00013601</td>
<td>1.2698693</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.03259429</td>
<td>2.0478339</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.01199044</td>
<td>4.023429</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.000197021</td>
<td>12.194172</td>
<td></td>
</tr>
</tbody>
</table>

* Reference 15.

This form has been used by a number of authors for similar calculations e.g., Refs. 3, 4, and 5.

1) Proof that $\langle \bar{a} | ZH_0 - HZ_0 | 0 \rangle = (E_\bar{a} - E_0) (\langle \bar{a} | Z | 0 \rangle)$$

Hence $H_0(0)$ is the projection onto the space spanned by the basis set.

2) If $\langle \bar{a} | ZH_0 | 0 \rangle = E_\bar{a} (\langle \bar{a} | Z | 0 \rangle)$

Hence $H_0(0)$ is the projection onto the space spanned by the basis set.

3) i.e., $\tilde{W}_i \geq \tilde{W}_i$.

4) Q.E.D.
LONG-RANGE RETARDED INTERACTION ENERGIES

\[
W_{\text{LLA2}} \text{[see Eq. (55) of Ref. 1]} \text{ the quadrupole terms } \varphi_{2m} \text{ were also included.}
\]

We have evaluated \( W_4 \) for the H–H, H–He, and He–He interactions. For the diagonalization of hydrogen we use as basis vectors the orbitals of Löwdin and Schull\(^9\) which are just orthonormal, linear combinations of the \( \varphi_{im} \) and form a complete discrete basis set.

For He, we used the \( \varphi_{im} \) directly where, following Chan and Dalgarno,\(^8\) the Hart and Herzberg\(^10\) 20-parameter wavefunction was used as \( \varphi_0 \) and as usual\(^9\) the substitution

\[
\langle F, \varphi_0 | H_0 - E_0 | F, \varphi_0 \rangle \approx \frac{1}{2} \sum_{i=1}^{\infty} \langle \varphi_i, \nabla F_i | \nabla F_i \rangle (16)
\]

was made.\(^11\)

The resulting \( W_4 \) for the interactions H–H, H–He, and He–He are listed in Table I. For this calculation a 10×10 matrix was diagonalized for hydrogen, and for helium,\(^12\) as we began to lose accuracy and computer time was becoming significant, only a 6×6 matrix was treated. It can also be seen from Table I that the Unsöld-type approximation suggested by Meath and Hirschfelder\(^4\) gives reasonable order of magnitude estimates for \( W_4 \). In addition we have listed in Table II the effective oscillator strengths and eigenfrequencies.\(^12\)

ACKNOWLEDGMENT

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APPENDIX

Simplified forms for most of the other coefficients of Ref. 1 can also be obtained. As the reductions are straightforward, only \( W_{\text{LLA2}} \) will be treated as it is more complicated than the others. The sum rules and second order energies necessary for the evaluation of the coefficients of Ref. 1 are listed in Table III and IV, and values for these coefficients are given in Table V. Numerical results for \( W_{\text{LLA3}} \) and \( W_{\text{LLA2}} \) have also been obtained, the latter required inclusion of quadrupole terms in Eq. (14).

For the coefficients of Paper II,

\[
U_5(a, b) = (\alpha^4/R^8) \sum (\alpha^4/R^8) \sum N_{na}(0) P_{na}^2 | 0 \rangle
\]

\[
+ | P_{na}^2 | 2 \rangle \langle 2 | P_{na}^2 | 0 \rangle \langle 0 | P_{na}^2 | 0 \rangle
\]

\[
U_6(a, b) = (\alpha^2/R^8) \sum N_{na}(0) P_{na}^2 | 0 \rangle
\]

\[
+ | P_{na}^2 | 2 \rangle \langle 2 | P_{na}^2 | 0 \rangle \langle 0 | P_{na}^2 | 0 \rangle
\]

\[
U_7(a, b) = (\alpha^2/R^8) \sum N_{na}(0) P_{na}^2 | 0 \rangle
\]

\[
+ | P_{na}^2 | 2 \rangle \langle 2 | P_{na}^2 | 0 \rangle \langle 0 | P_{na}^2 | 0 \rangle
\]

\[
U_8(a, b) = (\alpha^2/R^8) \sum N_{na}(0) P_{na}^2 | 0 \rangle
\]

\[
+ | P_{na}^2 | 2 \rangle \langle 2 | P_{na}^2 | 0 \rangle \langle 0 | P_{na}^2 | 0 \rangle
\]

\[
U_9(a, b) = (\alpha^2/R^8) \sum N_{na}(0) P_{na}^2 | 0 \rangle
\]

\[
+ | P_{na}^2 | 2 \rangle \langle 2 | P_{na}^2 | 0 \rangle \langle 0 | P_{na}^2 | 0 \rangle
\]

\[
U_{10}(a, b) = (\alpha^2/R^8) \sum N_{na}(0) P_{na}^2 | 0 \rangle
\]

\[
+ | P_{na}^2 | 2 \rangle \langle 2 | P_{na}^2 | 0 \rangle \langle 0 | P_{na}^2 | 0 \rangle
\]

And for \( W_{\text{LLA2}} \) of Paper I we have

\[
W_{\text{LLA2}} = 9/4(1+0_{ab}) \sum (\alpha_{na}^2 | 0 \rangle Q_{ab}^{\alpha_{na}} | 0 \rangle
\]

\[
+ 3/2 N_{na}(0) Z_{na}^2 | 0 \rangle \langle 0 | r_a^2 | r_b^2 | 0 \rangle
\]

\[
+ E_{\text{int}}(p_{za}, Q_{ab}^{\alpha_{na}}) + E_{\text{int}}(p_{za}, 2D_{ab}^{\alpha_{na}}) \langle 0 | P_{na}^2 | 0 \rangle \langle 0 | P_{na}^2 | 0 \rangle
\]

where

\[
Q_{ab}^{\alpha_{na}} = (6)^{-1/2} \sum_{i=1}^{\infty} (3Z_{ab}^2 - r_a^2)
\]

is the atomic quadrupole-moment operator,

\[
D_{ab}^{\alpha_{na}} = (6)^{-1/2} \sum_{i=1}^{\infty} (3Z_{ab}^2 - r_a^2)
\]

and the relation

\[
2 \langle j | D_{ab}^{\alpha_{na}} | 0 \rangle = \langle j | Q_{ab}^{\alpha_{na}} | 0 \rangle
\]

obtained from Eq. (34) of Ref. 1, holds.

\[
T^p(AB) = (6)^{-1/2}(-A \cdot B + 3A \cdot Z B_{ab})
\]

TABLE III. Dipole sum rules in atomic units, calculated using data of Table II, \( S_{i2} = \sum_j [A(j)]^2 j \cdot j \). (A7)

\[
\begin{array}{ccc}
\hline
 & & \\
 & H & He \\
\hline
\bar{S}_0 & 0.97 & 16.1 \\
\bar{S}_1 & 0.664 & 3.99 \\
\bar{S}_2 & 0.664 & 3.99 \\
\bar{S}_3 & 1.0 & 2.0 \\
\bar{S}_4 & 2.0 & 1.50479 \\
\bar{S}_5 & 4.5 & 1.37584 \\
\bar{S}_6 & 10.75 & 1.40312 \\
\bar{S}_7 & 26.8333 & 1.51963 \\
\bar{S}_8 & 67.17661 & 1.71285 \\
\bar{S}_9 & 172.18808 & 1.98161 \\
\hline
\end{array}
\]

\footnote{Reference 12.}

\footnote{Reference 15.}


\footnote{J. F. Hart and G. Herzberg, Phys. Rev. 106, 79 (1957).}

\footnote{That is, to the extent that \( H_4 = H_2 E_4 \), we have replaced \( H_4 \) by the Sternheimer Hamiltonian [J. M. Sternheimer, Phys. Rev. 96, 951 (1959)] and in particular Eq. (15) holds. Note however that to the same extent we no longer have strict upper bounds.}

\footnote{The larger basis set used here does not significantly effect the He refractive index calculation of Chan and Dalgarno, Y. M. Chan and A. Dalgarno, Proc. Phys. Soc. (London) 85, 227 (1965).}
The reduction of $W_{LL, A, 2}$ follows:

The expression Eq. (55)\(^1\) can be written as

$$W_{LL, A, 2} = \frac{1}{2} \sum_{j, k} \sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \left| \langle 0 | Z | k \rangle \right|^2 \left| \langle 0 | Q_0^p | k \rangle \right|^2 \frac{1}{\Delta_{E_0} \left( j + \Delta_{E_0} | k \right)}.$$

Using the identity of Eq. (3), Eq. (A12) becomes

$$W_{LL, A, 2} = (9.4) \left[ 1 + \sum_{j, k} \left( \Delta_{E_0} \left( j | E_0 | k \right) \right) \right] \left( \sum_{j, k} \sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \right),$$

where

$$[1] = \sum_{j, k} \sum_{j, k} \left[ \Delta_{E_0} \left( j | E_0 | k \right) \right]$$

and

$$[2] = -\sum_{j, k} \sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \left[ \Delta_{E_0} \left( j + \Delta_{E_0} | k \right) \right] \times \left| \langle 0 | Z | k \rangle \right|^2 \left| \langle 0 | Q_0^p | k \rangle \right|^2.$$

Using Eq. (A11) and Eq. (8), [2] is easily reduced to a second-order energy, as in the case of $W_{ll, 4}$,

$$[2] = -\sum_{j, k} \sum_{j, k} \left[ \frac{\langle 0 | Z | j \rangle \left| \langle 0 | Q_0^p | j \rangle \right|^2}{\Delta_{E_0} \left( j + \Delta_{E_0} | k \right)} \right] + \sum_{j, k} \sum_{j, k} \left[ \frac{\langle 0 | P_0 | j \rangle \left| \langle 0 | Q_0^p | j \rangle \right|^2}{\Delta_{E_0} \left( j + \Delta_{E_0} | k \right)} \right].$$

Or, in the previous notation

$$[2] = E^{(0)} \left( Z_0, 2D_0^p \right) + E^{(0)} \left( P_0, Q_0^p \right).$$

Now [1] can be simplified to

$$[1] = \frac{1}{2} \sum_{j, k} \sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \left| \langle 0 | Z^2 | k \rangle \right|^2 \left| \langle 0 | Q_0^p | k \rangle \right|^2,$$

where the last term is in the form of a quadrupole sum rule. To evaluate this sum, applying Eq. (A11), we write

$$\sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \left| \langle 0 | Z^2 | k \rangle \right|^2 \left| \langle 0 | Q_0^p | k \rangle \right|^2. = -\sum_{k} \sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \left| \langle 0 | Q_0^p | k \rangle \right|^2 \left| \langle 0 | Z | k \rangle \right|^2.$$

Using the expressions for $Q_0^p$ and $D_0^p$ from Eq. (A9) and Eq. (A10), the commutator becomes

$$[Q_0^p, D_0^p] = \frac{1}{3} \sum_{k=1}^{N} \left[ 3Z^2 + r^2 \right]$$

Therefore, for spherically symmetric ground states,\(^4\)

$$\sum_{j, k} \sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \left| \langle 0 | Z^2 | k \rangle \right|^2 \left| \langle 0 | Q_0^p | k \rangle \right|^2 = \frac{1}{3} \sum_{k=1}^{N} \sum_{j, k} \left( \langle 0 | r^2 | k \rangle \right)$$

$$= \frac{1}{3} \sum_{j, k} \sum_{j, k} \left( \langle 0 | r^2 | k \rangle \right).$$

Whereby, Eq. (A15) for [1] becomes, using Eqs. (A16) and (A17),

$$[1] = -\sum_{j, k} \sum_{j, k} \Delta_{E_0} \left( j | E_0 | k \right) \left| \langle 0 | Z^2 | k \rangle \right|^2 \left| \langle 0 | Q_0^p | k \rangle \right|^2 + \frac{1}{3} \sum_{j, k} \sum_{j, k} \left( \langle 0 | r^2 | k \rangle \right).$$

Combining (A18) and (A14) one obtains the desired expression Eq. (A8) for $W_{LL, A, 2}$. This expression can be evaluated like $W_{ll, 4}$, obtaining an upper bound with knowledge of the ground-states wavefunctions for the isolated atoms.


\(^2\) Effective quadrupole matrix elements and energy differences for hydrogen are available on request from the authors, as are the second-order energies in $W_{LL, 4}$. 