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Nonadiabatic Long-Range Forces

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A general expression is obtained for the leading long-range correction to the static interaction of a slowly moving charged or neutral system at a large distance from a spherically symmetric atom, and precise estimates are presented of the magnitude for the systems H, He (1S, 2S, and 2P), Ne, Ar, Kr, Xe, Li, Na, K, Rb, Cs, H₂, Ne₂, and CH₄.

I. INTRODUCTION

Some years ago, Dalgarno and McCarroll¹ derived an expression for the leading asymptotic correction to the static interaction of a slowly moving charge of arbitrary mass at a large distance from a hydrogen atom, and recently, Kleinman, Hahn, and Spruch,² Opik,³ and Callaway et al.⁴ have derived an expression for the case of a slowly moving electron interacting with any spherically symmetric atom. It is a straightforward matter to extend the analysis of Dalgarno and McCarroll to the general case of any charged or neutral particle interacting with any other. The resulting formulas involve dipole oscillator strengths, and various techniques can be employed to obtain accurate estimates of the asymptotic nonadiabatic forces for all cases of interest.

II. THEORY

The Schrödinger equation for a system of N electrons of mass m and of two other particles A and B of masses M_A and M_B, respectively, is

\[\left(-\frac{\hbar^2}{2\mu}\sum_{i=1}^{N} \nabla_i^2 - \frac{\hbar^2}{2M_A} \nabla_A^2 - \frac{\hbar^2}{2M_B} \nabla_B^2 + V\right)\Psi = E\Psi, \tag{1}\]

where the potential V is a function of the inter-particle separations \(\mathbf{r}_i \mathbf{r}_j\), \(\mathbf{r}_i\) being the position vector of the \(i\)th particle. When the motion of the center of mass of the entire system is separated out and all positions are referred to the center of mass of A and B, Eq. (1) becomes

\[\left[-\frac{\hbar^2}{2\mu}\nabla_i^2 + \mathbf{R}\right]\Phi = E\Phi, \tag{2}\]

where \(\mathbf{R} \equiv \sum_{i=1}^{N} m_i \mathbf{r}_i / (M_A + M_B)\), \(\mathbf{r}_i\) is the vector from A to B and

\[H = -\frac{\hbar^2}{2\mu} \sum_{i=1}^{N} \nabla_i^2 - \frac{\hbar^2}{2M_A} \sum_{i\neq j} \nabla_i \cdot \nabla_j + V, \tag{3}\]

\(\mu\) being the reduced mass \(m_0 A_B / (m_A + m_B)\). The Hamiltonian H has eigenfunctions \(\chi_i(\mathbf{R}, \mathbf{r}_i)\) and eigenvalues \(E_i(\mathbf{R})\), which depend parametrically on \(\mathbf{R}\). Expand \(\Phi(\mathbf{R}, \mathbf{r}_i)\) according to

\[\Phi(\mathbf{R}, \mathbf{r}_i) = \sum_{i} F_i(\mathbf{R}) \chi_i(\mathbf{R}, \mathbf{r}_i), \tag{4}\]

multiply by \(\chi_i^*(\mathbf{R}, \mathbf{r}_i)\), and integrate over the configuration space of all the electrons. It follows that

\[\left[T + E_i(\mathbf{R}) - E\right]F_i(\mathbf{R}) + \sum_{i' \neq i} C_{i'i} F_{i'}(\mathbf{R}) = 0, \tag{5}\]

where \(T = -\hbar^2 / 2(3\mu) \nabla_i^2\),

and \(C_{i'i} = -\hbar^2 / 2(3\mu) \int \chi_i^* \nabla_i \nabla_i d\mathbf{r} \cdot \nabla R + \int \chi_i \nabla_i \nabla_i d\mathbf{r}\). \(\tag{6}\)

If the coupling terms \(C_{i'i}\) are neglected, Eq. (5) is the Born-Oppenheimer approximation. If the diagonal term

\[C_{ii} = \int \chi_i^* T R \chi_i d\mathbf{r} \tag{7}\]

is retained, Eq. (5) reduces to

\[\{T + [E_i(\mathbf{R}) + E_{ii}(\mathbf{R})] - E\} F_i(\mathbf{R}) = 0, \tag{8}\]

so that the particles A and B can be regarded as moving in an effective field \(E_i(\mathbf{R}) + E_{ii}(\mathbf{R})\). The correction \(E_{ii}(\mathbf{R})\) is that recently derived by Kleinman et al.² and described by them as the nonadiabatic correction. It was described by Dalgarno and McCarroll as the adiabatic correction, the term nonadiabatic referring to the influence of the off-diagonal coupling terms.

Kleinman et al.² proceeded by decomposing the total wave function \(\Phi(\mathbf{R}, \mathbf{F})\) into \(P\Phi + Q\Phi\), where \(P\) is the projection operator \(\chi_0(\mathbf{R}, \mathbf{F})\). Then,

\[\{T + E_0(\mathbf{R}) + E_{00}(\mathbf{R}) - E\} F_0(\mathbf{R}) = \chi_0 \{T Q(\mathbf{R}) (E - Q\mathbf{H}Q) - 1 \} Q T_R \chi_0 \{P F_0(\mathbf{R})\} \tag{9}\]

Kleinman et al.² then demonstrated that the non-local potential on the right-hand side of Eq. (10)
decreased asymptotically as $R^{-n}$ for the case when system $A$ consists of a single electron and $B$ is a spherically symmetric atom. We shall offer here an alternative derivation and slightly extend their result.

At large distances $R$, the system is assumed to separate into two spherically symmetric systems in their ground states, one of which has $n_A$ electrons associated with particle $A$ and the other of which has $n_B$ electrons associated with particle $B$. The eigenfunctions of the separated systems satisfy the equations

$$ H_A \psi_A^m = E_A^m \psi_A^m, $$

and

$$ H_B \phi_B^n = E_B^n \phi_B^n. $$

At distances such that the wave functions of $A$ and $B$ do not overlap, we can write

$$ \langle \chi_t | T_R | \chi_t \rangle = \psi_A^m(\mathbf{r}_A) \phi_B^n(\mathbf{r}_B) \times \left( 1 - \frac{1}{2} \sum_{m,n} \left( \frac{\psi_A^m(\mathbf{r}_A) \phi_B^n(\mathbf{r}_B)}{(E_A^m + E_B^n)} \right)^2 \right) \left( \sum_{m,n} \frac{\psi_A^m(\mathbf{r}_A) \phi_B^n(\mathbf{r}_B)}{(E_A^m + E_B^n)} \right) + O(R^{-4}), $$

in which the perturbation $H - H_A - H_B$ can be written as a power series in $R^{-1}$ according to

$$ H - H_A - H_B = \sum_i R^{-i} \psi_i(\mathbf{r}_A) \phi_i(\mathbf{r}_B). $$

If system $A$ is charged with an excess charge $Z_A e$ and $B$ is neutral, Eq. (13) can be written

$$ H - H_A - H_B = \frac{Z_A e^2}{R^2} \sum i = 1 \frac{z_i B}{R^2} + O(R^{-4}), $$

where $(x_i B, y_i B, z_i B)$ are the Cartesian coordinates of electron $i$ referred to $B$, and the $z$ axis is chosen parallel to $R$. Then, using Eqs. (13) and (15), we obtain asymptotically

$$ \langle \chi_t | T_R | \chi_t \rangle = - \frac{e^2}{2m} (2Z_A^2 / R^2) \left( \frac{1}{R^2} \right) \sum_{m,n} \frac{\psi_A^m(\mathbf{r}_A) \phi_B^n(\mathbf{r}_B)}{(E_A^m + E_B^n)} \right)^2 + O(R^{-9}). $$

Introducing the dipole oscillator strength

$$ f_n(B) = \left( \frac{2m}{\hbar} \right)^2 \frac{2}{E_B^n - E_B^0} \left( \sum_{i=1}^{n_B} \frac{1}{z_i B} \right) \left( \frac{1}{E_B^n - E_B^0} \right)^2, $$

we can write

$$ \langle \chi_t | T_R | \chi_t \rangle = - \frac{e^2}{2m} \frac{Z_A^2 e^6}{R^6} \left( \frac{1}{E_B^n - E_B^0} \right)^2 \sum_{m,n} f_n(B) \left( \frac{1}{E_A^m - E_B^n} \right)^2. $$

If particle $A$ is an electron, $M_A = m = m$ and we obtain the correction term

$$ e^2 \left( \frac{2m}{m} \right)^2 \sum_{i=1}^{n_B} \sum_{j=1}^{n_A} \frac{(x_i B \times y_j A + y_i B \times x_j A)}{(E_B^n - E_B^0)} + 2 \frac{(x_i B \times z_j A + z_i B \times x_j A)}{(E_B^n - E_B^0)}, $$

and we obtain

$$ \langle \chi_t | T_R | \chi_t \rangle = - \frac{e^2}{2} \left( \frac{2m}{m} \right)^3 \sum_{i=1}^{n_B} \sum_{j=1}^{n_A} \frac{(x_i B \times y_j A + y_i B \times x_j A)}{(E_B^n - E_B^0)} + 2 \frac{(x_i B \times z_j A + z_i B \times x_j A)}{(E_B^n - E_B^0)}, $$

Consider now the off-diagonal coupling terms in Eq. (5) for the case when excitation is not energetically possible, so that

$$ R F_0(\mathbf{R}) = 0 \text{ as } R \to \infty $$

for $t = 0$. For a charged particle colliding with a spherically symmetric atom, it follows from Eqs. (14) and (15) that $u^{(t)}$ decreases at least as fast as $R^{-4}$. Thus

$$ S^{(t)} \langle \mathbf{F}_0(\mathbf{R}) \rangle = e^{-t} F_0(\mathbf{R}) + O(R^{-5}). $$

Then, adopting an argument used by Castillero, Percival, and Seaton and noting that $F_i(\mathbf{R})$ decreases at least as fast as $R^{-3}$, we can show that

$$ F_i(\mathbf{R}) \to \frac{e^{-t} F_0(\mathbf{R})}{E_B^0 - E_B^i} + O(R^{-5}). $$

Hence

$$ S^{(t)} \langle \mathbf{F}_0(\mathbf{R}) \rangle = e^{-t} F_0(\mathbf{R}) + O(R^{-5}). $$

The operator $|e^{(t)} F_0(\mathbf{R})|^2$ contains terms decreasing as $R^{-3}$, $R^{-5} \phi / \Phi$, and $R^{-3} \phi / \Phi^2$. For bound states, $F_0(\mathbf{R})$ decreases exponentially. For con-
tinum states $\varphi E_n/\varphi R \sim k E_n/R$ and $\varphi^2 E_n/\varphi R^2 \sim k^2 E_n/R^2$,
where $k^2 = 2m(E - E_F)/\hbar^2$.

Similar arguments can be applied to the scattering of neutral spherically symmetric atoms to show that the leading terms of the nonlocal potential behave asymptotically as $R^{-10}$, $kR^{-6}$, and $k^2R^{-8}$.

### III. EVALUATION OF THE COEFFICIENTS

Kleinman et al.\(^2\) have presented a table of upper and lower bounds to the summation

$$\beta_1 = \frac{1}{2} \sum_n f_n \left[ (E_n - E_0)^3 \right],$$

(26)

for He, Li, Ne, and Na. A variety of sources exist that can be used to make precise predictions of $\beta_1$ and of

$$\gamma_1 = \frac{1}{2} \sum_n f_n \left[ (E_n - E_0^0) (E_n - E_0)^2 \right] - 1,$$

(27)

for these and for other atoms and molecules.

The coefficient $\beta_1$ can be written in atomic units in the form

$$\beta_1 = \frac{1}{2} \int \chi_1 | \vec{r}, \omega = 0 \rangle \rangle \vec{r}, \omega \rangle d\vec{r},$$

(28)

where $(H - E_0^1 + \omega) \chi_1 + \sum_i \vec{r}_i \psi_0 = 0.$

If we introduce also $\kappa_i$ by the equation

$$(H - E_0^1 - \omega) \kappa_i + \sum_i \nabla \chi_i = 0,$$

(29)

and define

$$\Phi(\omega, \omega') = \int \chi_1 | \vec{r}, \omega \rangle \kappa_1 | \vec{r}, \omega' \rangle d\vec{r},$$

(30)

$$\gamma_1 \text{ can be written as:}$$

$$\gamma_1 = \frac{1}{4\pi} \int_0^\infty d\omega d\omega' \int_0^\infty d\omega' \Phi_A(\omega, \omega') \Phi_B(\omega, \omega'),$$

(31)

Atomic Hydrogen

For a hydrogen ion in its ground state, $\chi_1$ is known exactly,\(^3\) with the result that $\beta_1 = (43/8Z^2) a_0^4$, where $Z$ is the nuclear charge.

### Helium

Precise variational calculations of $\chi_1$ have been reported for helium on several occasions. Values of $\beta_1$ can be derived immediately from the data of Chan and Dalgarno\(^7\) and of Victor, Dalgarno, and Taylor.\(^8\) In units of $a_0^4$, the values are 0.702 and 0.706, respectively. A semi-empirical value of 0.705, has been reported by Bell and Kingston.\(^9\)

A two-term fit to refractive index data\(^10\) yields 0.73, and the series representation of refractive index data by Dalgarno and Kingston\(^11\) gives a value of 0.708.\(^3\) An estimate of $\beta_1$ can also be derived from Hartree–Fock perturbation theory.\(^12\) The uncoupled approximation leads to a value of 0.767, and the coupled approximation to 0.656, the errors being comparable to those occurring in Hartree–Fock calculations of the dipole polarizability.

### Metastable Helium

The accurate variational calculations of $\chi_1$ for He(21S) and He(22S) yield values of $\beta_1$ of 1.76 x $10^{-3} a_0^4$ and 3.63 x $10^{-3} a_0^4$, respectively, to within a probable error of 3%.

### Lithium Positive Ion

Accurate variational calculations\(^14\) of $\chi_1$ for Li\(^+\), Li\(^+(21S), \) and Li\(^+(22S)\) yield values of $\beta_1$ of 3.5 x $10^{-3} a_0^4$, 9.97 x $10^{-3} a_0^4$, and 2.72 x $10^{-3} a_0^4$, respectively to within a probable error of 1%.

### Lithium

A variational calculation of $\chi_1$ for Li has been carried out to somewhat lower accuracy than have calculations for two-electron systems.\(^15\) The resulting value of $\beta_1$ is 1.18 x $10^{-3} a_0^4$, accurate probably to within an error of 5%. The value is in harmony with a semi-empirical value of 1.2 x $10^{-3}$, which can be derived from the tabulation of Dalgarno and Davison.\(^16\)

### Alkali Metals

Dalgarno and Davison's tabulation yields immediately semi-empirical values of 1.1 x $10^{-3} a_0^4$, 2.5 x $10^{-3} a_0^4$, 2.7 x $10^{-3} a_0^4$, and 3.8 x $10^{-3} a_0^4$ for Na, K, Rb, and Cs, respectively. The error is controlled by the uncertainty in the oscillator strength of the first resonance transition; it can be as large as 20% for Cs.

### Inert Gases

Semi-empirical values of $\beta_1$ for the inert gases have been listed by Bell and Kingston\(^8\) and by Opik.\(^9\) We have obtained alternative estimates from the representations of refractive index data used by Dalgarno, Morrison, and Pengelly,\(^10\) and a comparison is presented in Table I. The comparison suggests that the use of refractive-index

<table>
<thead>
<tr>
<th>Gas</th>
<th>Bell and Kingston(^8)</th>
<th>Opik(^9)</th>
<th>Refractive-index data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>1.27</td>
<td>1.26</td>
<td>1.28</td>
</tr>
<tr>
<td>Ar</td>
<td>8.33</td>
<td>7.99</td>
<td>5.52</td>
</tr>
<tr>
<td>Kr</td>
<td>14.50</td>
<td>13.17</td>
<td>14.9</td>
</tr>
<tr>
<td>Xe</td>
<td>29.15</td>
<td>24.4</td>
<td>28.9</td>
</tr>
</tbody>
</table>
alone is usually sufficient to give estimates of $\beta_1$ to within an uncertainty of 5%.

Molecules

Semi-empirical values of $8.92a_0^4$ and $5.03a_0^4$, respectively, can be derived from sets of oscillator strengths for $N_2$, $H_2$, and $H_2$ and of $9.1a_0^4$, $5.1a_0^4$, and $17.3a_0^4$, respectively, from refractive-index data on $N_2$, $H_2$, and $CH_4$. The sets of oscillator strengths for $H_2$ can be used to distinguish between the parallel and perpendicular contributions to $\beta_1$. They are, respectively, $6.69a_0^4$ and $4.20a_0^4$.

Table II is a collection of recommended values for all the cases we have considered. The error is usually less than 5%; in no case should it exceed 20%.

Because of the mass $M$ in the denominator of Eq. (21), the long-range adiabatic correction for neutral systems appears to have only little more than formal interest. In Table III we present results for $\gamma_1$ for mixtures of helium with the light elements $H$, $H_2$, $He$, and $Li$.

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**Table II.** Recommended values of $\beta_1$ in units of $a_0^4$.

<table>
<thead>
<tr>
<th>Atom or molecule</th>
<th>$\beta_1$</th>
<th>Atom or molecule</th>
<th>$\beta_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$ (1S)</td>
<td>5.375</td>
<td>Rb</td>
<td>$2.7 \times 10^3$</td>
</tr>
<tr>
<td>He (2S)</td>
<td>0.706</td>
<td>Cs</td>
<td>$3.8 \times 10^3$</td>
</tr>
<tr>
<td>He (2P)</td>
<td>$1.76 \times 10^4$</td>
<td>Ne</td>
<td>1.27</td>
</tr>
<tr>
<td>He (2F)</td>
<td>$3.64 \times 10^3$</td>
<td>Ar</td>
<td>8.33</td>
</tr>
<tr>
<td>Li$^+$(1S)</td>
<td>$3.53 \times 10^2$</td>
<td>Kr</td>
<td>$1.45 \times 10^2$</td>
</tr>
<tr>
<td>Li$^+$ (2S)</td>
<td>$9.97 \times 10^3$</td>
<td>Xe</td>
<td>$2.92 \times 10^2$</td>
</tr>
<tr>
<td>Li</td>
<td>$2.72 \times 10^3$</td>
<td>H$_2$</td>
<td>6.69</td>
</tr>
<tr>
<td>Li$^+$ (2P)</td>
<td>$1.18 \times 10^3$</td>
<td>H$_2$</td>
<td>4.20</td>
</tr>
<tr>
<td>Na</td>
<td>$1.1 \times 10^3$</td>
<td>N$_2$</td>
<td>8.92</td>
</tr>
<tr>
<td>K</td>
<td>$2.4 \times 10^3$</td>
<td>CH$_4$</td>
<td>$1.73 \times 10^3$</td>
</tr>
</tbody>
</table>

---

**Table III.** Values of $\gamma_1$ in units of $a_0^5$ for He interacting with $H$, $H_2$, $He$, and $Li$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\gamma_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$</td>
<td>1.27</td>
</tr>
<tr>
<td>$H_2$</td>
<td>2.06</td>
</tr>
<tr>
<td>$He$</td>
<td>1.48</td>
</tr>
<tr>
<td>$Li$</td>
<td>0.46</td>
</tr>
</tbody>
</table>

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* National Research Council Visiting Research Associate.