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Nonadiabatic Long-Range Forces

A. Dalgarno
Smithsonian Institution Astrophysical Observatory, and
Harvard College Observatory, Cambridge, Massachusetts

G. W. F. Drake*
Smithsonian Institution Astrophysical Observatory, Cambridge, Massachusetts

and

G. A. Victor
Technology Division, GCA Corporation, Bedford, Massachusetts
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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 (1^1S, 2^1S, and 2^3S), Ne, Ar, Kr, Xe, Li^+ (1^1S, 2^1S, and 2^3S), Li, Na, K, Rb, Cs, H_2, N_2, and CH_4.

I. INTRODUCTION

Some years ago, Dalgarno and McCarroll[1] 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] Öpik,[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

$$\left(-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2-\frac{\hbar^2}{2M_A}\nabla_A^2-\frac{\hbar^2}{2M_B}\nabla_B^2+V\right)\Psi=\mathcal{E}\Psi, \quad (1)$$

where the potential V is a function of the interparticle separations $\vec{r}_i-\vec{r}_j$, $\vec{r}_i$ being the position vector of the ith 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

$$[-(\hbar^2/2\mathfrak{M})\nabla_R^2+H]\Phi=E\Phi, \quad (2)$$

where $M=M_A+M_B$, $\mathfrak{M}=M_AM_B/M$, $\vec{R}$ is the vector from A to B and

$$H=-\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\nabla_i^2-\frac{\hbar^2}{2M}\sum_{i\neq j}\nabla_i\cdot\nabla_j+V, \quad (3)$$

μ being the reduced mass $m\mathfrak{M}/(m+\mathfrak{M})$. The Hamiltonian H has eigenfunctions $\chi_t(\vec{R},\vec{r}_i)$ and eigenvalues $E_t(\vec{R})$, which depend parametrically on $\vec{R}$.

Expand $\Phi(\vec{R},\vec{r}_i)$ according to

$$\Phi(\vec{R},\vec{r}_i)=\mathbf{S}_t F_t(\vec{R})\chi_t(\vec{R},\vec{r}_i), \quad (4)$$

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

$$[T_R+E_t(\vec{R})-E]F_t(\vec{R})+\mathbf{S}_{t'}\mathcal{C}_{tt'}F_{t'}(\vec{R})=0, \quad (5)$$

$$\text{where } T_R=-(\hbar^2/2\mathfrak{M})\nabla_R^2, \quad (6)$$

$$\text{and } \mathcal{C}_{tt'}=-(\hbar^2/2\mathfrak{M})\Big(2\int\chi_t^*\nabla_R\chi_{t'}d\vec{r}\cdot\nabla_R+\int\chi_t\nabla_R^2\chi_{t'}d\vec{r}\Big). \quad (7)$$

If the coupling terms $\mathcal{C}_{tt'}$ are neglected, Eq. (5) is the Born-Oppenheimer approximation. If the diagonal term

$$\mathcal{C}_{tt}(\vec{R})=\int\chi_t^*T_R\chi_t\,d\vec{r} \quad (8)$$

is retained, Eq. (5) reduces to

$$\{T_R+[E_t(\vec{R})+\mathcal{C}_{tt}(\vec{R})]-E\}F_t(\vec{R})=0, \quad (9)$$

so that the particles A and B can be regarded as moving in an effective field $E_t(\vec{R})+\mathcal{C}_{tt}(\vec{R})$. The correction $\mathcal{C}_{tt}(\vec{R})$ is that recently derived by Kleinman *et al.*[2] and described by them as the nonadiabatic correction. It was described by Dalgarno and McCarroll[1] 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 $\Phi(\vec{R},\vec{r})$ into $P\Phi+Q\Phi$, where P is the projection operator $|\chi_0(\vec{R},\vec{r})\rangle\times\langle\chi_0(\vec{R},\vec{r})|$. Then,

$$[T_R+E_0(\vec{R})+\mathcal{C}_{00}(\vec{R})-E]F_0(\vec{R})=\langle\chi_0|T_RQ(E-QHQ)^{-1}QT_R|\chi_0\rangle F_0(\vec{R}). \quad (10)$$

Kleinman *et al.*[2] then demonstrated that the nonlocal potential on the right-hand side of Eq. (10)

decreased asymptotically as R^{-8} 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

$$H_A\psi_A^{\,m} = E_A^{\,m}\psi_A^{\,m}, \tag{11}$$

and

$$H_B\phi_B^{\,n} = E_B^{\,n}\phi_B^{\,n}. \tag{12}$$

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

$$\chi_t(\vec{\mathrm{R}},\vec{\mathrm{r}}_i) = \psi_A^{\,0}(\vec{\mathrm{r}}_i)\phi_B^{\,0}(\vec{\mathrm{r}}_j)$$

$$\times\left(1-\frac{1}{2}\mathop{\mathbf{S}'}_{m}\mathop{\mathbf{S}'}_{n}\frac{|\langle\psi_A^{\,0}\phi_B^{\,0}|H-H_A-H_B|\psi_A^{\,m}\phi_B^{\,n}\rangle|^2}{[(E_A^{\,0}+E_B^{\,0})-(E_A^{\,m}+E_B^{\,n})]^2}\right)$$

$$+\mathop{\mathbf{S}'}_{m}\mathop{\mathbf{S}'}_{n}\frac{\langle\psi_A^{\,0}\phi_B^{\,0}|H-H_A-H_B|\psi_A^{\,m}\phi_B^{\,n}\rangle\langle\psi_A^{\,m}\phi_B^{\,n}|}{(E_A^{\,0}+E_B^{\,0})-(E_A^{\,m}+E_B^{\,n})}$$

$$+O((H-H_A-H_B)^2), \tag{13}$$

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

$$H-H_A-H_B=\textstyle\sum_l R^{-l}\,V_l(\hat{R},\hat{r}_i). \tag{14}$$

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

$$H-H_A-H_B=\frac{Z_Ae^2}{R^2}\sum_{i=1}^{n_B} z_{iB}+O(R^{-3}), \tag{15}$$

where (x_{iB}, y_{iB}, z_{iB}) are the Cartesian coordinates of electron i referred to B, and the z axis is chosen parallel to $\vec{\mathrm{R}}$. Then, using Eqs. (13) and (15), we obtain asymptotically

$$\langle\chi_t|T_R|\chi_t\rangle = -(\hbar^2/2\mathfrak{M})(6Z_A^{\,2}e^4/R^6)$$

$$\times\mathop{\mathbf{S}'}_{n}\left|\left\langle\phi_B^{\,0}\middle|\sum_{i=1}^{n_B}z_{iB}\middle|\phi_B^{\,n}\right\rangle\right|^2/(E_B^{\,0}-E_B^{\,n})^2$$

$$+O(R^{-9}). \tag{16}$$

Introducing the dipole oscillator strength

$$f_n(B)=(2m/\hbar^2e^2)(E_B^{\,n}-E_B^{\,0})$$

$$\times\left|\left\langle\phi_B^{\,0}\middle|\sum_{i=1}^{n_B}z_{iB}\middle|\phi_B^{\,n}\right\rangle\right|^2, \tag{17}$$

we can write

$$\langle\chi_t|T_R|\chi_t\rangle=-\frac{3}{2}\frac{\hbar^2}{\mathfrak{M}m}\frac{Z_A^{\,2}e^6}{R^6}\mathop{\mathbf{S}'}_{n}\frac{f_n(B)}{(E_B^{\,n}-E_B^{\,0})^3}. \tag{18}$$

If particle A is an electron, $M_A=\mathfrak{M}\simeq m$ and we obtain the correction term

$$\mathcal{C}_{tt}=-\frac{3}{2}\frac{(h^2e^2/m)^2}{R^6}\mathop{\mathbf{S}'}_{n}\frac{f_n(B)}{(E_B^{\,n}-E_B^{\,0})^3}, \tag{19}$$

which is identical to the expression derived by Kleinman *et al*.[2]

For neutral atoms A and B,

$$H-H_A-H_B=\frac{e^2}{R^3}\sum_{i=1}^{n_B}\sum_{j=1}^{n_A}(x_{iB}x_{jA}+y_{iB}y_{jA}$$

$$+2z_{iB}z_{jA})+O(R^{-4}), \tag{20}$$

and we obtain

$$\langle\chi_t|T_R|\chi_t\rangle=-\tfrac{45}{4}(h^2e^2/m)^3e^2(m/\mathfrak{M})$$

$$\times\frac{1}{R^8}\mathbf{S}'\,\mathbf{S}'f_m(A)f_n(B)$$

$$\times[(E_A^{\,m}-E_A^{\,0})(E_B^{\,n}-E_B^{\,0})$$

$$\times(E_A^{\,m}-E_A^{\,0}+E_B^{\,n}-E_B^{\,0})^2]^{-1}$$

$$+O(R^{-11}). \tag{21}$$

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

$$RF_t(\vec{\mathrm{R}})\to 0 \quad\text{as}\quad R\to\infty \tag{22}$$

for $t\neq 0$. For a charged particle colliding with a spherically symmetric atom, it follows from Eqs. (14) and (15) that $\mathcal{C}_{tt'}$ decreases at least as fast as R^{-4}. Thus

$$\mathbf{S}_{t'}\,\mathcal{C}_{tt'}F_{t'}(\vec{R})\sim\mathcal{C}_{t0}F_0(\vec{\mathrm{R}})+O(R^{-5}). \tag{23}$$

Then, adopting an argument used by Castillejo, Percival, and Seaton[5] and noting that $E_t(\vec{\mathrm{R}})$ decreases at least as fast as R^{-2}, we can show that

$$F_t(\vec{\mathrm{R}})\sim-\,\mathcal{C}_{t0}F_0(\vec{\mathrm{R}})/(E_B^{\,0}-E_B^{\,t})+O(R^{-5}). \tag{24}$$

Hence

$$\mathop{\mathbf{S}}_{t}\mathcal{C}_{0t}F_t(\vec{\mathrm{R}})\sim-\mathop{\mathbf{S}}_{t}\frac{|\mathcal{C}_{t0}|^2}{E_B^{\,0}-E_B^{\,t}}F_0(\vec{\mathrm{R}})+O(R^{-9}). \tag{25}$$

The operator $|\mathcal{C}_{t0}|^2$ contains terms decreasing as R^{-8}, $R^{-7}\,\partial/\partial R$, and $R^{-6}\,\partial^2/\partial R^2$. For bound states, $F_0(\vec{R})$ decreases exponentially. For continuum states,[2] $\partial F_0/\partial R \sim kF_0(\vec{R})$ and $\partial^2 F_0/\partial R^2 \sim k^2 F_0(\mathrm{R})$, where $k^2 = 2M(E - E_B{}^0)/\hbar^2$.

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^{-9}, 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

$$\beta_1 = \tfrac{1}{2} \mathbf{S}_n{}' f_n/(E^n - E^0)^3, \tag{26}$$

for He, Li, Ne, and Na. A variety of sources exist that can be used to make precise predictions of β_1 and of

$$\gamma_1 = \mathbf{S}_m{}' \mathbf{S}_n{}' f_m(A) f_n(B)[(E_A{}^m - E_A{}^0) \times (E_B{}^n - E_B{}^0)(E_A{}^m - E_A{}^0 + E_B{}^n - E_B{}^0)^2]^{-1}, \tag{27}$$

for these and for other atoms and molecules.

The coefficient β_1 can be written in atomic units in the form

$$\beta_1 = \tfrac{1}{2}\int |\chi_1(\vec{\mathrm{r}}, \omega = 0)|^2 d\vec{\mathrm{r}}, \tag{28}$$

where
$$(H - E^0 \pm \omega)\chi_1 + \sum_{i=1}^{m} \vec{\mathrm{r}}_i \psi^0 = 0. \tag{29}$$

If we introduce also ζ_1 by the equation

$$(H - E^0 - \omega)\zeta_1 + \sum_{i=1}^{n} \nabla_i \psi^0 = 0, \tag{30}$$

and define

$$\begin{aligned}\Phi(\omega,\omega') = {} & \int \chi_1(\vec{\mathrm{r}}, i\omega)\zeta_1(\vec{\mathrm{r}}, i\omega')d\vec{\mathrm{r}} \\ & + \int \chi_1(\vec{\mathrm{r}}, i\omega)\zeta_1(\vec{\mathrm{r}}, -i\omega')d\vec{\mathrm{r}} \\ & + \int \chi_1(\vec{\mathrm{r}}, -i\omega)\zeta_1(\vec{\mathrm{r}}, i\omega')d\vec{\mathrm{r}} \\ & + \int \chi_1(\vec{\mathrm{r}}, -i\omega)\zeta_1(\vec{\mathrm{r}}, -i\omega')d\vec{\mathrm{r}},\end{aligned} \tag{31}$$

γ_1 can be written

$$\gamma_1 = \frac{1}{4\pi^2}\int_0^\infty d\omega \int_0^\infty d\omega' \Phi^A(\omega,\omega')\Phi^B(\omega,\omega'). \tag{32}$$

Atomic Hydrogen

For a hydrogen ion in its ground state, χ_1 is known exactly,[6] with the result[1,2] that $\beta_1 = (43/8Z^6)\, a_0{}^4$, where Z is the nuclear charge.

Helium

Precise variational calculations of χ_1 have been reported for helium on several occasions. Values of β_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_5 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 β_1 can also be derived from Hartree-Fock perturbation theory.[12,13] 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 χ_1 for He(2^1S) and He(2^3S) yield values of β_1 of $1.76 \times 10^4 a_0{}^4$ and 3.63×10^3,[8] respectively, to within a probable error of 3%.

Lithium Positive Ion

Accurate variational calculations[14] of χ_1 for Li$^+$, Li$^+$(2^1S), and Li$^+$(2^3S) yield values of β_1 of $3.5 \times 10^{-2} a_0{}^4$, $9.97 \times 10^2 a_0{}^4$, and $2.72 \times 10^2 a_0{}^4$, respectively to within a probable error of 1%.

Lithium

A variational calculation of χ_1 for Li has been carried out to somewhat lower accuracy than have calculations for two-electron systems.[15] The resulting value of β_1 is $1.18 \times 10^3 a_0{}^4$, accurate probably to within an error of 5%. The value is in harmony with a semi-empirical value of 1.2×10^3, 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 $1.1 \times 10^3 a_0{}^4$, $2.5 \times 10^3 a_0{}^4$, $2.7 \times 10^3 a_0{}^4$, and $3.8 \times 10^3 a_0{}^4$ 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 β_1 for the inert gases have been listed by Bell and Kingston[9] and by Öpik.[3] 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 I. Values of β_1 for the inert gases in units of $a_0{}^4$.

Gas	Bell and Kingston[9]	Öpik[3]	Refractive-index data
Ne	1.27	1.26	1.28
Ar	8.33	7.99	8.52
Kr	14.50	13.17	14.9
Xe	29.15	24.4	28.9

TABLE II. Recommended values of β_1 in units of a_0^4.

Atom or molecule	β_1	Atom or molecule	β_1
H	5.375	Rb	2.7×10^3
He (1^1S)	0.706	Cs	3.8×10^3
He (2^1S)	1.76×10^4	Ne	1.27
He (2^3S)	3.64×10^3	Ar	8.33
Li^+ (1^1S)	3.53×10^{-2}	Kr	1.45×10
Li^+ (2^1S)	9.97×10^2	Xe	2.92×10
Li^+ (2^3S)	2.72×10^2	$H_2 \parallel$	6.69
Li	1.18×10^3	$H_2 \perp$	4.20
Na	1.1×10^3	N_2	8.92
K	2.4×10^3	CH_4	1.73×10

alone is usually sufficient to give estimates of β_1 to within an uncertainty of 5%.

Molecules

Semi-empirical values of $8.92 a_0^4$ and $5.03 a_0^4$, respectively, can be derived from sets of oscillator strengths for N_2[17] and H_2,[18] and of $9.1 a_0^4$, $5.1 a_0^4$, and $17.3 a_0^4$, respectively, from refractive-index data on N_2, H_2, and CH_4.[7] The sets of oscillator strengths for H_2 can be used to distinguish between the parallel and perpendicular contributions to β_1. They are, respectively, $6.69 a_0^4$ and $4.20 a_0^4$.

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 $\mathfrak{M}$ 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 γ_1 for mixtures of helium with the light elements H, H_2, He, and Li.

TABLE III. Values of γ_1 in units of a_0^6 for He interacting with H, H_2, He, and Li.

Gas	γ_1
H	1.27
H_2	2.06
H_2	1.48
He	0.46
Li	13.98

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[*] National Research Council Visiting Research Associate.

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