Nonadiabatic Corrections to the Method of Perturbed Stationary States*

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Using the method of perturbed stationary states, nonadiabatic corrections to the cross section for symmetric resonant charge exchange between a proton and a hydrogen atom in its ground state are induced by considering the role played by the $2P^0$ state. These corrections lead to a polarization of the electron cloud induced by the relative motion of the hydrogen-proton systems. Such effects are found to be important for the calculation of the differential cross section, but are found to play a minor role in determining the value of the total cross section.

I. INTRODUCTION

THE problem of the charge exchange of an electron from a state i in a system A to a state j in system B has been treated, to say the least, rather extensively in the literature. The simplest case of this is electron transfer between a proton and a hydrogen atom:

$$H^++H(1S) \rightarrow H+H^+$$
.

When the velocity of relative motion of the protons greatly exceeds that of the electron in the 1S state, high-velocity approximations such as the first Born approximation and the impact-parameter formulation become complicated and also questionable (because they neglect back-coupling to the initial state, for example). However, at relative velocities much less than that of the electron, it seems quite reasonable to treat the calculation of the total cross section in an adiabatic approximation; i.e., to treat the entire system as a quasihydrogen-molecular ion.

II. ADIABATIC TREATMENT

In the incident energy range of about a keV, the protons may be treated as classical particles, as $\hbar/m_p v \ll a_0$, the Bohr radius, and it is assumed that the screening is sufficient so that the incident proton moves in a straight line in the laboratory system. This is well substantiated by experiment, as the differential cross section is strongly peaked about the forward scattering angles.²

The Hamiltonian for the system at a given instant is taken to be

$$H = -\frac{1}{2}\nabla^2 + e^2[1/R - 1/r_1 - 1/r_2], \qquad (1)$$

where $\hbar = m_e = 1$, and the relative position vectors **R**, \mathbf{r}_1 , and \mathbf{r}_2 are shown in Fig. 1.

The "molecular"-state wave functions are taken to be symmetric and antisymmetric eigenfunctions of the static system, but include effects of the translational motion of the protons; after Bates¹:

$$\varphi_s^{\pm} = \frac{1}{2} \left[(X_s^+ + X_s^-) \exp(-\frac{1}{2} i \mathbf{v} \cdot \mathbf{r}) \right]$$

$$\pm (X_s^+ - X_s^-) \exp(+\frac{1}{2} i \mathbf{v} \cdot \mathbf{r}) \exp(-\frac{1}{8} i v^2 t), \quad (2)$$

 X_s^+ and X_s^- being the exact eigenfunctions of the Hamiltonian, Eq. (1). The complete wave function is expanded in terms of the φ_s 's:

$$\bar{\Psi}(t) = \sum_{s} \left\{ C_{s}^{+}(t) \varphi_{s}^{+}(t) \exp \left[-i \int_{-\infty}^{t} E_{s}^{+}(\mathbf{R}) dt \right] + C_{s}^{-}(t) \varphi_{s}^{-}(t) \exp \left[-i \int_{-\infty}^{t} E_{s}^{-}(\mathbf{R}) dt \right] \right\}.$$
(3)

Applying $(H-i\hbar\partial/\partial t)=0$, orthogonality, and the symmetry of the $\varphi_s^{\pm 2}$ s, Bates obtains sets of coupled differential equations. For example, if the sum is just taken over s=0, 1 (1S and 2P states), one would obtain:

$$-i\dot{C}_0{}^{+}S_{00}{}^{+} + C_0{}^{+}T_{00}{}^{+} + C_1{}^{+}T_{01}{}^{+} = 0, \tag{4}$$

$$-i\dot{C}_1 + S_{11} + C_1 + T_{11} + C_0 + T_{10} + = 0, (5)$$

(and a similar set of equations from the antisymmetric part of $\overline{\Psi}$);

$$S_{mm}^{\pm} = 1 \pm \frac{1}{2} \int \{X_m^{+*} X_m^{+} - X_m^{-*} X_m^{-}\} \cos(\mathbf{v} \cdot \mathbf{r}) d^3 r;$$

$$T_{mn}^{\pm} = \left\{ \pm (E_n^{-} - E_n^{+}) \int X_m^{\mp} * X_n^{\mp} \sin^2(\frac{1}{2} \mathbf{v} \cdot \mathbf{r}) d^3 \mathbf{r} \right\}$$
 (6)

$$\pm \nu_{mn} + it_{mn}^{\pm}$$
 exp $\left[i \int_{-t}^{t} (E_m^{\pm} - E_n^{\pm}) dt \right];$

$$\nu_{mn} = \frac{1}{4} \int \left\{ (X_m^{+*} + X_m^{-*}) \frac{\partial}{\partial t} (X_n^{+} - X_n^{-}) \right\}$$

$$-(X_m^{+*}-X_m^{-*})\frac{\partial}{\partial t}(X_n^{+}+X_n^{-})\bigg\}\sin(\mathbf{v}\cdot\mathbf{r})d^3r. \quad (7a)$$

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¹ See, for example, D. R. Bates and R. McCarrol, Advan. Phys. 2, 39 (1962) for a rather comprehensive summary and an exhaustive list of references.

² G. J. Lockwood and E. Everhart, Phys. Rev. **125**, 567 (1962) did experiments measuring the differential cross section for large-

angle scattering in this energy range.

See, also, William Lichten, Phys. Rev. 131, 229 (1963) who examined this data. The breakdown of the adiabatic approximation at these small impact parameters is shown to take place owing to the interference of other atomic and molecular states for most processes. For the one being considered here, however, he finds the approximation to be quite good (which gives Fig. 2 a firmer foundation).

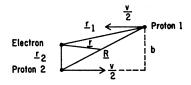


Fig. 1. Geometry of resonant charge-exchange process.

The term v_{mn} in curly brackets entering the expression T_{mn}^{\pm} subtracts out to zero when added to its negative contribution in the adiabatic treatment. The antisymmetric functions of R are it_{mn}^{+} and also cancel out in the adiabatic treatment. It is easily shown that it_{01}^{+} and it_{10}^{+} are the predominant terms which give the contribution for the nonadiabatic corrections included in this paper. They arise from those it_{mn}^{\pm} which have the form

$$-\int X_m^{\pm *} \frac{\partial}{\partial t} X_n^{\pm} \cos^2 \left(\frac{\mathbf{v} \cdot \mathbf{r}}{2}\right) d^3 r. \tag{7b}$$

The adiabatic treatment essentially consists in considering m=n=0, and dropping terms of order $(v/e^2)^2$ and higher:

$$H^++H(IS) \rightarrow H(IS)+H^+$$
.

This implies, using Eqs. (4) and (5), that $C_0^+(-\infty) = C_0^-(-\infty) = C_0^+(\infty) = C_0^-(\infty) = 1/\sqrt{2}$.

The probability for finding the electron on proton 2 at $R=\infty$, it being initially on proton 1, is

$$P = \frac{1}{4} \left| \int d^3r \{ \varphi_0^{+*} - \varphi_0^{-*} \} \left\{ \varphi_0^{+} \exp\left(-i \int_{-\infty}^{\infty} E_0^{+} dt \right) + \varphi_0^{-} \exp\left(-i \int_{-\infty}^{\infty} E_0^{-} dt \right) \right\} \right|^2 = \sin^2 \xi, \quad (8)$$

where

$$\xi = \int_{-\infty}^{\infty} (E_0^+ - E_0^-) dt. \tag{9}$$

Until now, previous work on this problem have been concerned with finding suitable analytic expressions for $E_0^+ - E_0^-$ which would produce as nearly as possible energies calculated in the static limit using exact wave functions of the hydrogen molecular ion³ for the $1S\sigma_g$ and the $2P\sigma_u$ states corresponding to E_0^+ and E_0^- , respectively. Static polarization effects have been considered taking into account the distortion of the electron cloud about proton 1 due to the presence of proton 2. In what follows, interest will be focused on velocitydependent polarization corrections from the coupling of higher angular-momentum states (such as the $2S\sigma_g$ and the $3P\sigma_u$ states) due to virtual excitations caused by the relative motion of the two protons. To measure the size of these correction terms, it is most convenient to calculate the S_{mn}^{\pm} and the T_{mn}^{\pm} terms of Eqs. (6) and (7) using asymptotic leao (linear combination of atomic

orbitals) wave functions to represent the correct $X_s^{\pm 2}$'s of Eq. (2). To be consistent, we must of course calculate $E_0^+ - E_0^-$ by the same procedure. Using asymptotic wave functions for the Hamiltonian given in Eq. (1), $E_0^+ - E_0^-$ can be calculated:

$$\Psi_0^+ = \frac{\exp(-r_1) + \exp(-r_2)}{(2\pi)^{1/2} (1 + I_{00})^{1/2}};$$

$$I_{00} = \int \exp\{-(r_1 + r_2)\} d^3r.$$
(10)

In units of the rydberg $(-e^2/2a_0)$,

$$E_0^+ - E_0^- = (4/R)\{\frac{1}{3}2R^2 - 1\} \exp(-R)$$

to a very good approximation. Looking at Fig. 1,

$$\partial/\partial t = R(\partial/\partial R) + (b/R^2)iL_x,$$
 (11)

where iL_x is the rotation operator corresponding to an apparent rotation of the protons about the intersection of \mathbf{r} and \mathbf{R} . For velocities of the incident proton much less than that of the electron in its orbit $(v \ll (e^2 a_0)/c)$, the term iL_x can be neglected. Also, it is seen to couple only states of the same angular momentum and different magnetic quantum numbers, and in this theory will not couple the 1S state to any others. Therefore, we have

$$d/dt = (dR/dt)(d/dR), (12)$$

and

$$\frac{dR}{dt} = \frac{\{R^2 - b^2\}^{1/2}}{R} \frac{1}{v}.$$
 (13)

With R in units of a_0 ; v in units of v/e^2 , Eq. (9) becomes

$$\xi = \frac{1}{v} \int_{b}^{\infty} dR \, \frac{4}{R} \left\{ 1 - \frac{2R^{2}}{3} \right\} \, \exp(-R) \frac{R}{\{R^{2} - b^{2}\}^{1/2}} \,. \tag{14}$$

This integral is sharply peaked about R=b, and gives

$$\xi \simeq (-4/v)(2\pi/b)^{1/2} \exp(-b)\{\frac{1}{3}b^2 + \frac{1}{3}b - \frac{1}{4}\}.$$
 (15)

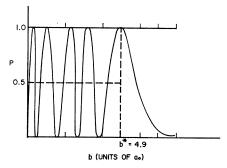


Fig. 2. Probability of charge transfer P as calculated in the adiabatic approximation, as a function of impact parameter h.

² D. R. Bates, H. S. W. Massey, and A. L. Stewart, Proc. Roy. Soc. (London) A216, 437 (1953).

The cross section is obtained from

$$\sigma = \frac{\pi}{2} b^{*2} + 2\pi \int_{b^*}^{\infty} db \ b \sin^2 \xi(b) \,, \tag{16}$$

where b^* is taken to be the largest value of b for which the probability has a maximum (see Fig. 2). In this scheme it is evident that the asymptotic representation Eq. (10) is well justified.

The scattering of protons on hydrogen atoms has been done in the laboratory by Fite et al.4 As the experiment has an error of some 15%, obviously more data must be accumulated before judgment is finally passed on the theory of perturbed stationary states in the region of 1 keV. Figure 3 shows the results of previous calculations⁵ using modified linear-combination-ofatomic-orbitals wave functions described by Eq. (2) for the $1S\sigma_u$ and $2P\sigma_u$ states to obtain values of $E_0^+-E_0^-$. Calculations were performed⁵ to include the velocitydependent terms multiplying $E_0^+ - E_0^-$, entering via the T_{00}^{\pm} terms. The results shown clearly do not bring experiment and theory into closer agreement. It should be remarked that the method of evaluating the cross section Eq. (16) is open to interpretation and scrutiny, especially as its value seems to be quite sensitive to b^* . But, of course, the physical principles involved do seem quite sound in this energy region; it is this puzzle that leads to a search for some corrections or at least to a clue as to the range of applicability of the method.

III. NONADIABATIC CORRECTIONS

For these reasons, a more careful examination of Eqs. (4) and (5) seems in order. The $2P^0$ state is included because of its long range which mathematically may extend the curve in Fig. 2 to larger values of b, and physically may account for some velocity-induced polarization of the electron cloud as the second proton passes by. As will be included here, the $(2P^0)$ velocitydependent polarization effects tend to increase the cross section (back towards the experimental values).

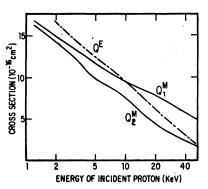
As $v \to 0$, S_{00}^{\pm} and S_{11}^{\pm} go to 1, to order Kv^2 where Kis a constant of order 1. At 1 keV, v = 0.2, and thus S_{00}^{\pm} may be taken to be 1 to within a few percent for this

 T_{00}^{\pm} and T_{11}^{\pm} enter as phase factors to C_0^{\pm} and C_1^{\pm} , respectively. T_{00}^{\pm} would replace ξ by $\xi + \delta$ in Eq. (9):

$$\xi + \delta = \int_{-\infty}^{\infty} dt (E_0^+ - E_0^-) + \int_{-\infty}^{\infty} dt (T_{00}^+ - T_{00}^-). \quad (17)$$

Similarly, T_{11}^{\pm} alter the coefficients C_1^{\pm} , which are already assumed small, by an order of v^2 . From Eq. (7), $(T_{00}^+ - T_{00}^-)$ is seen to be of order $K_1v^2(E_0^+ - E_0^-)$, where K_1 is of order 1 and therefore this correction also amounts to at most a few percent, and can be neglected.

Fig. 3. Q^E is the experimental curve; Q_1^M is the calculated cross section, and Q_2^M is the calcula- Q_2^M including the T_{00}^{\pm} terms. $(Q_1^M$ and Q_2^M have approximations to the exact eigenfunctions of the Hamiltonian, Eq. (1), different from the asymptotic wave functions used here.)



The effects of T_{01}^{\pm} and T_{10}^{\pm} remain to be calculated. The series of approximations which follow tend to somewhat overestimate this correction.

The equations to be solved are

$$-i\dot{C}_0 + C_1 + T_{01} = 0,$$

$$-i\dot{C}_1 + C_0 + T_{10} = 0,$$
(18)

(with similar equations for the antisymmetric coeffi-

Full expressions for T_{01}^+ and T_{10}^+ are

$$T_{01}^{+} = (\Psi_0^{+}, d\Psi_1^{+}/dt) \exp(i\Delta^{+}),$$

$$T_{10}^{+} = (\Psi_1^{+}, d\Psi_0^{+}/dt) \exp(-i\Delta^{+}),$$
(19)

where

$$\Delta^{+} = \int_{-}^{t} (E_0^{+} - E_1^{+}).$$

Asymptotic wave functions are again employed using Eq. (10) for the (IS) state; and for the 2P state,

$$\Psi_{1}^{+} = \frac{\mathbf{r}_{1} \cdot \mathbf{R} \exp(-\mathbf{r}_{1}/2) - \mathbf{r}_{2} \cdot \mathbf{R} \exp(-\mathbf{r}_{2}/2)}{R[2(32)\pi]^{1/2}[1 - I_{11}]^{1/2}} -\Psi_{0}^{+}(\Psi_{0}^{+}, \varphi_{1}^{+}) = \varphi_{1}^{+} - \Psi_{0}^{+}(\Psi_{0}^{+}, \varphi_{1}^{+}). \quad (20)$$

By orthogonality, $(\Psi_0^+, \Psi_1^+) = 0$ leads to

$$-\left(\Psi_{0}^{+}, \frac{d}{dt}\Psi_{1}^{+}\right) = \left(\Psi_{1}^{+}, \frac{d}{dt}\Psi_{0}^{+}\right) = (+); \qquad (21)$$

analogously, one defines

$$(-) = \left(\Psi_1^-, \frac{d}{dt}\Psi_0^-\right).$$

From Eq. (10)

$$\Psi_0^+ = \frac{-dI_{00}/dt}{2(1+I_{00})} \times \Psi_0^+$$

$$-\frac{dR}{dt} \left\{ \frac{\mathbf{R} \cdot \mathbf{r}_1}{Rr_1} \exp(-r_1) - \frac{\mathbf{R} \cdot \mathbf{r}_2}{Rr_2} \exp(-r_2) \right\} - \dots (22)$$

⁴ W. L. Fite, R. F. Stebbings, D. G. Hummer, and R. T. Brackmann, Phys. Rev. 119, 663 (1960).
⁵ A. F. Ferguson, Proc. Roy. Soc. (London) A264, 540 (1961).

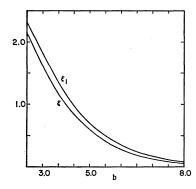


Fig. 4. The argument of sin², the probability distribution, as a function of b at v = 0.5.

It remains to solve for $C_0^+(\infty)$

$$C_0^+(\infty) = -i \int_{-\infty}^{\infty} dt(+) \exp(i\Delta^+)$$

$$\times \int_{-\infty}^{t} dt(+) \exp(-i\Delta^+) C_0^+. \quad (23)$$

For all finite t in the integrand, (+) and C_0^+ are smooth functions of R(t) compared to the rapidly oscillating phase factors $e^{\pm i\Delta^+}$. The major contribution to $C_0^+(\infty)$ occurs from regions where $e^{i\Delta^+}$ can cancel $e^{-i\Delta^+}$. Therefore, an approximate expression can be found for $C_0^{\pm}(\infty)$

$$C_0^{+}(\infty) = -\frac{1}{\sqrt{2}} \exp\left(-i \int_{-\infty}^{\infty} dt \frac{(+)^2}{(E_0^{+} - E_1^{+})}\right). \quad (24)$$

One can similarly obtain for $C_1^+(\infty)$,

$$C_1^+(\infty) = -\frac{1}{\sqrt{2}} \int_{-\infty}^{\infty} dt (+) e^{-i\Delta^+}.$$
 (25)

Here, there is no cancellation of the rapidly oscillating phase factor and the expression for $C_1^+(\infty)$ is cancelled out as K_2v , where K_2 is of order 0. Its contribution to the probability would, of course, come in as the second power. This clearly illustrates that the reaction being dealt with is a resonance charge transfer, and not an ionization process due to the large energy gap between the n=1 and n=2 states.²

 ξ in Eq. (9) is now replaced by ξ_1 :

$$\xi_{1} = \int_{-\infty}^{\infty} dt \left\{ E_{0}^{+} - E_{0}^{-} + \frac{(+)^{2}}{(E_{0}^{+} - E_{1}^{+})} - \frac{(-)^{2}}{(E_{0}^{-} - E_{1}^{-})} \right\}. \quad (26)$$

The energies are given in terms of $-e^2/2a_0$ by

$$E_{0}^{\pm} = 1 - \frac{2}{R} + \frac{2(G_{00} \pm J_{00})}{(1 \pm I_{00})},$$

$$E_{1}^{\pm} = \frac{1}{4} - \frac{2}{R} + \frac{2(G_{11} \mp J_{11})}{(1 \mp I_{11})},$$
(27)

where G_{00} , I_{00} , J_{00} are evaluated in a paper by N. Rosen⁶ [see Eqs. (A1) in Appendix].

The integrals G_{11} , I_{11} , J_{11} can be gotten from the same paper by replacing ρ by $\rho/2$ [see Eqs. (A2)].

Using Eqs. (20), (21), and orthogonality [and dropping $(\psi_0^+, d\psi_1/dt)$

$$(+) = \frac{-I_{01} - I_{00}}{\frac{dt}{2(I + I_{00})}}$$

$$-\frac{\frac{dR}{dt} \int d^{3}\mathbf{r} \left\{ \frac{\mathbf{r}_{1}\mathbf{R}}{r_{1}R} \exp(-r_{1}) - \frac{\mathbf{r}_{2}\mathbf{R}}{r_{r}R} \exp(-r_{2}) \right\}}{16\pi\sqrt{2}(1 - I_{11})^{1/2}}$$

$$\times \frac{\left\{ \frac{\mathbf{r}_{1}\mathbf{R}}{R} \exp(-r_{1}/2) - \frac{\mathbf{r}_{2}\mathbf{R}}{R} \exp(-r_{2}/2) \right\}}{(1 + I_{00})^{1/2}}. \quad (28)$$

 I_{01} can be calculated by setting $\epsilon = \frac{1}{2}$ in the integral I_{01} in a paper by B. N. Dickinson⁷ [See Eq. (A3)]. I_{01} was found by evaluating $\int d^3r \exp(-r_1)(r_2\mathbf{R}/R) \exp(-\frac{1}{2}r_2)$, in elliptic coordinates. The second term on the righthand side was also done in this manner, using prolate spheroid transformations. The result may be found in Eq. (A6). Factoring dR/dt out of (+) and (-),

$$\xi_{1} = 2 \int_{b}^{\infty} dR \left(\frac{1}{v} \frac{R}{(R^{2} - b^{2})^{1/2}} (E_{0}^{+} - E_{0}^{-}) + \frac{v(R^{2} - b^{2})^{1/2}}{R} \left\{ \frac{(+)^{2}}{(E_{0}^{+} - E_{0}^{+})} - \frac{(-)^{2}}{(E_{0}^{-} - E_{1}^{-})} \right\} \right). \quad (29)$$

The quantities $(\xi_1 - \xi)$ and σ [Eq. (16)] were obtained by numerical integration.

IV. CONCLUSION

The long-range contributions to the probability from the $2P^0$ state become increasingly important as the velocity increases:

It appears that the adiabatic theory is no longer valid as a perturbation treatment in powers of v, even for v as small as 0.3, if information about the differential cross section is desired. To emphasize the contribution of the velocity-induced polarization effects, the corrected argument of the \sin^2 function ξ_1 is contrasted to the adiabatic-argument ξ in Fig. 4 for v = 0.5.

The situation is more palatable if the cross section is calculated: For this process, it therefore seems consistent to calculate the cross section with the adiabatic theory in an expansion of (v/e^2) . (It should be noted that the asymptotic approximation gives a cross section

⁶ N. Rosen, Phys. Rev. **38**, 2099 (1931).

⁷ B. N. Dickinson, J. Chem. Phys. **1**, 137 (1933).

Table I. Effects of velocity-dependent polarization corrections to the probability of resonant charge exchange for various values of the impact parameters at different incident relative proton velocities.

$\left(\frac{v}{e^2}\right)$	Impact parameter (units of a_0)	sin² <i>Ę</i>	$\sin^2\! {\it E}_1$	% correction
	4.9	1.00	0.997	a
0.2	8.0	0.020	0.022	10.0
	4.3	0.999	0.984	8
0.3	6.5	0.096	0.117	22.0
	3.5	0.998	0.938	a
0.5	5.0	0.308	0.421	37.0

a Sin2 £1 has not yet reached its maximum.

Table II. Effects of velocity-dependent polarization corrections to the total cross section for resonant charge exchange at different relative proton velocities.

$\left(\frac{v}{e^2}\right)$	σ (Adiabatic) (units of $10^{-16}~{\rm cm^2}$)	σ (with $2p$ correction included)	% correction
0.2 0.3	21.1 18.2	21.3 18.9	1.0 3.7
0.5	14.8	16.0	8.1

larger than that calculated with more realistic wave functions.)

Tables I and II show that contributions from higher states are important even in resonant charge transfer processes, even for moderately small velocities. These contributions suggest a strong distortion of the electron cloud, very sensitive to the incident proton velocity which prohibits the use of static wave functions for the calculations of probabilities and differential cross sections in low- and moderate-velocity regions, and of total cross sections in moderate-velocity regions. This latter restriction is, of course, expected as in this range the incident proton velocity becomes comparable to that of the velocity of the electron in its first Bohr orbit; and the exact static electron wave functions, Ψ_0^{\pm} (and Ψ_1^{\pm} , of course) of the Hamiltonian, Eq. (1), can no longer be considered as time-averaged functions of r_1 and r_2 , but in general will be an explicit function of the time t. The former restriction, however, forces one to consider in greater detail the actual physical processes taking place if one wants to obtain a decent theoretical interpretation for resonant charge exchange at a fixed value of the impact parameter.

ACKNOWLEDGMENT

The author is indebted to Professor K. A. Brueckner for suggesting this problem and for several enlightening discussions during the calculation and preparation of this work.

APPENDIX

From N. Rosen⁶

$$G_{00} = 1/R - \exp(-2R)(1+1/R),$$

 $I_{00} = \exp(-R)(R^2/3 + R + 1),$ (A1)
 $J_{00} = \exp(-R)(R + 1).$

Putting $\rho \to \rho/2$ for the 2P integrals in the same paper,

$$G_{11} = 1/R + 12/R^{3} - (\exp(-R)/R) \times \left[\frac{1}{8}R^{3} + \frac{3}{4}R^{2} + 11R/4 + 7 + 12/R + 12/R^{2}\right],$$

$$I_{11} = \exp(-\frac{1}{2}R) \times \left[R^{4}/240 + R^{3}/60 - R^{2}/20 - \frac{1}{2}R - 1\right],$$

$$J_{11} = \frac{1}{4}\exp(-R/2)\left[R^{3}/24 - \frac{1}{2}R - 1\right].$$
Setting $\epsilon = \frac{1}{2}$ in I_{01} in the paper by B. N. Dickinson,⁷

$$I_{01} = (\frac{4}{3})^{4}\sqrt{2}\left[-\exp(-r)\{6 + 12/R + 12/R^{2}\} + \exp(-R/2)\{9R/16 - 3 + 6/R + 12/R^{2}\}\right].$$
(A3)

The integra

$$\int d^{3}\mathbf{r} \left\{ \frac{\mathbf{r}_{1} \cdot \mathbf{R}}{r_{1}R} \exp(-r_{1}) - \frac{\mathbf{r}_{2} \cdot \mathbf{R}}{r_{2}R} \exp(-r_{2}) \right\}$$

$$\times \left\{ \frac{\mathbf{r}_{1} \cdot \mathbf{R}}{R} \exp(-r_{1}/2) - \frac{\mathbf{r}_{2} \cdot \mathbf{R}}{R} \exp(-r_{2}/2) \right\} \quad (A4)$$

was evaluated in prolate spheroid coordinates:

$$\mathbf{r}_{1} = \mathbf{r} - \frac{1}{2}\mathbf{R} = \frac{1}{2}R(x+y),$$

$$\mathbf{r}_{2} = \mathbf{r} + \frac{1}{2}\mathbf{R} = \frac{1}{2}R(x-y),$$

$$d^{3}r = (2\pi/8)R^{3}(x^{2} - y^{2})dxdy,$$

$$\mathbf{r}_{1} \cdot \mathbf{R} = -\frac{1}{2}R^{2}(xy+1),$$

$$\mathbf{r}_{2} \cdot \mathbf{R} = -\frac{1}{2}R^{2}(xy-1).$$
(A5)

The answer is

512/81+
$$\left[\exp\left(-\frac{1}{2}R\right)(16R/9)\left\{216(4/3R)^4+144(4/3R)^3+156(4/3R)^2-44(4/3R)+8\right\}$$

- $\exp\left(-R\right)(64/27)\left\{216(4/3R)^3+288(4/3R)^2+192(4/3R)+32\right\}$ (A6)