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Impact-parameter method for proton–hydrogen-atom scattering variational bounds on the 1s charge-exchange amplitudes*

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A trial wave function that is a linear combination of two traveling hydrogenlike basis functions which contain two variable-charge parameters and a polarization parameter has been used to obtain bounds on the second-order error term in the variational principles of Demkov and Storm that are comparable to the magnitudes of approximate 1s charge-exchange amplitudes. It is demonstrated that the error function $\Delta_1(X_i)$ can be employed to judge various calculations and as an aid in adjusting parameters in the trial wave function to obtain better bounds. Based upon the use of Δ_1 as a measure of error in an approximate trial wave function, we conclude that the Euler-Lagrange variational method is not the optimal approach. Suggestions are made for future work which might improve the calculated bounds.

I. INTRODUCTION

The proton–hydrogen-atom scattering problem is one of the simplest three-body problems involving the rearrangement of atomic particles. Furthermore, in the important intermediate energy range, roughly specified as 1–100 keV, this three-body problem can be reasonably simplified by the adoption of the semiclassical impact-parameter approximation. Despite the simplicity of the impact-parameter model system, it has not been possible to solve the time-dependent Schrödinger equation for the impact-parameter wave function.

Approximate solutions are customarily generated by expressing an approximate or trial wave function as a linear combination of a finite number of square-integrable basis functions. The most popular basis has been the set of traveling hydrogenic orbitals introduced by Bates and McCarroll.[1] However, as Wilets and Gallaher[2] observed, trial wave functions expressed in terms of these basis functions lack sufficient flexibility to adequately represent the exact impact-parameter wave function during the middle of the collision. The Sturmian[3] and pseudostate[4] basis sets were introduced in an attempt to deal with this defect. However, trial wave functions constructed with these types of basis functions cannot in general satisfy the boundary conditions imposed by the asympotic forms of the exact impact-parameter wave function.[5] Furthermore, in the pseudostate method, one introduces an artificiality by including arbitrary functions. For example, Cheshire, Gallaher, and Taylor[4] included arbitrary functions which are for all time approximate representations of the lower bound states of the helium ion. These difficulties could be avoided by adopting the more powerful approach apparently suggested to Wilets and Gallaher[2] by Russek. The flexibility in the trial wave function could be increased by including time-dependent variable parameters in the basis functions, and these parameters would be continuously adjusted to change so that the atomiclike character required for large $|t|$ is continuously changed into molecularlike character as the two protons approach. Cheshire developed a variational framework in which to exploit this suggestion,[6] and the approach, which has been referred to as the Euler-Lagrange variational method, is based on the requirement that the functional considered by Sil[7] be stationary. Cheshire[6] and McCarroll, Piacentini, and Salin[8] have investigated the case of time-dependent nuclear charge parameters in the 1s traveling hydrogenlike basis functions. Although Cheshire's method is really not variational in the sense that the functional is stationary for the types of variations represented by available trial wave function,[9,10] the approximate transition amplitudes ultimately obtained are second-order accurate.[10,11] Other variational methods have been suggested[10,12] and recently applied.[13]

By following an indirect variational approach, it is possible, *in principle*, to obtain exact impact-parameter transition amplitudes. Spruch[14] and later Storm[10,15] derived upper and lower variational bounds that bracket the exact amplitudes, and thus by adjusting the parameters in these bounds, one can, at least in principle, bracket the amplitudes as closely as desired. An error function which is a measure of the error associated with the trial wave function has been introduced.[15] The absolute values of the errors in the approximate transition amplitudes are uniformly bounded by the magnitude of the error function.

One can, as we shall demonstrate, use the error function to judge various calculational approaches, and as an aid in the adjustment of the parameters in the trial wave function to yield better bounds.

A preliminary report which gave the magnitudes of the variational bounds for some simple trial wave functions has been published.[16] The purpose of the present work is to describe the calculation in greater detail, present new results, and, based on this exploratory work, attempt to assess the future success of this indirect approach. In Sec. II, we develop the theory for the proton–hydrogen-atom case and briefly comment upon its application to more complex ion-atom collisions. The calculational procedures are discussed in Sec. III, and the results and suggestions for future work are discussed in Sec. IV. It should be pointed out that although the basic conclusions stated in our preliminary report remain unchanged, the previously reported magnitudes of the error function and approximate 1s charge-exchange amplitudes have been modified somewhat as a result of a more accurate account of some matrix elements and the inclusion of the contribution to the error function which comes from the integration from a large positive time to infinity.

II. THEORETICAL DEVELOPMENT

Let the position of proton 2 with respect to proton 1 be given by $\vec{R}(t)$, and let the positions of the electron with respect to proton 1, proton 2, and the midpoint of $\vec{R}(t)$ be given by $\vec{r}_1$, $\vec{r}_2$, and $\vec{r}$. Three right-handed coordinate systems are chosen as follows: First, as discussed by Bates,[17] it is necessary to choose a stationary coordinate system with origin at the midpoint of $\vec{R}(t)$; for convenience the axes are aligned so that the relative motion of the two protons takes place in the y-z plane: Therefore

$$\vec{R}(t) = b\hat{y} + vt\hat{z}, \tag{1}$$

where b is the impact parameter and v is the velocity of the incident proton. Second, it is convenient to choose two rotating coordinate systems with origins at the two protons, and with z axes directed in the $\hat{R}(t)$ direction.

One then seeks the solution to the time-dependent Schrödinger equation:

$$i\left(\frac{\partial}{\partial t}\right)_{\vec{r}} \psi_i = H(t)\psi_i, \tag{2}$$

which has the following asymptotic forms[18]:

$$\begin{aligned} &\psi_i \sim \phi_i^T e^{-i\epsilon_i t} \quad \text{as } t \to -\infty, \\ &\psi_i \sim \sum_n (\delta_{ni} + A_{ni})\phi_n^T e^{-i\epsilon_n t} \quad \text{as } t \to \infty, \end{aligned} \tag{3}$$

where the subscript i denotes the initial state from which the state vector ψ_i evolves. The Hamiltonian in Eq. (2) is

$$H = -\tfrac{1}{2}\nabla_r^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}, \tag{4}$$

and it can be expressed as

$$H = h_1 - 1/r_2 + 1/R = h_2 - 1/r_1 + 1/R, \tag{5}$$

where h_i is the Hamiltonian for the hydrogen atom with proton i as the nucleus. The asymptotic forms of the wave function are expressed in Eq. (3) in terms of the states of the Schrödinger time representation in which excitation is most conveniently described; these dynamical states are[18]

$$\phi_n^T = T\phi_n, \tag{6}$$

where T is the unitary operator corresponding to the translation of the origin from proton 1 to the midpoint of $\vec{R}(t)$. The quantities ϕ_n and ϵ_n are eigenvalues and eigenfunctions of the hydrogen-atom Hamiltonian h_1, and the A_{ni} are the impact-parameter amplitudes for the transitions from the initial state ϕ_i to the final states ϕ_n. For discrete indices n, the A_{ni} correspond to the amplitudes for excitation. The impact-parameter wave function can also be expressed in terms of the dynamical states of the time representation in which charge exchange is most conveniently described; in this case the unperturbed states are $\{\phi_{n2}^T\}$.[18]

In order to obtain approximate transition amplitudes, one must select a trial wave function X_i that belongs to the class of functions that have the same asymptotic forms as ψ_i. Consider trial wave functions expressed as a two-centered linear combination of parametrized traveling hydrogenlike orbitals:

$$X_i = \sum_{k=1}^{2} \sum_{nk=1}^{N} C_{nk,i}(t)\,\chi_{nk}(\xi_{nk}), \tag{7}$$

where the ξ_{nk} parameters in the basis functions χ_{nk} are restricted by the requirement that the basis functions approach traveling hydrogenic orbitals as $|t| \to \infty$. Trial wave functions such as those of Eq. (7) belong to the set of acceptable trial wave functions, since in the limit $|t| \to \infty$ the states ϕ_n^T or ϕ_{n2}^T approach traveling orbitals, and bound states on different centers are orthogonal. Since the variational principles given by Demkov,[19] Spruch,[14] and Storm[10] require that the dynamical states of the system, in this case the set $\{\phi_n^T\}$ or equivalently the set $\{\phi_{n2}^T\}$, be known, it might appear that these variational principles, and the variational bounds which follow from them, would not be applicable when two-centered traveling hydrogenlike trial wave functions are employed. However, it can be easily demonstrated that the variational principles of Demkov[19] and Storm[10] are applicable for trial wave functions in the form of Eq. (7) since the basis functions χ_{nk} approach ϕ_n^T or ϕ_{n2}^T in the limit $|t| \to \infty$, and bound states on different centers are orthogonal in this limit. In particular one can obtain the result[20]

$$A_{nk,i} = C_{nk,i} - iR(X_{nk,R}, X_i) + i\Delta(\delta\psi_{nk,R}, \delta\psi_i), \qquad (8)$$

where $X_{nk,R}$ is a time-reversed trial wave function that approaches the state ϕ_{nk}^T as $|t| \to \infty$, and $\delta\psi_{nk,R}$ is the error in this trial wave function. Although it is not obvious, it appears that Spruch's variational principles[14] could be extended to the class of trial wave functions represented by Eq. (3) by the same type of argument.

By neglecting the unknown second-order term Δ, the right-hand side of Eq. (8) provides a second-order accurate estimate of the exact transition amplitudes. Of interest, therefore, is an estimate of the error in the multitude of approximate transition amplitudes that could be generated in this manner with trial wave functions X_{nR} and X_i. If the trial wave functions remain normalized for all time, it can be shown by using the Schwartz inequality that

$$|A_{nk,i} - C_{nk,i} + iR(X_{nk}, X_i)| \le \beta\Delta_1, \qquad (9)$$

where in general $\beta = 2$ and Δ_1 is the error function[15]:

$$\Delta_1 = \int_{-\infty}^{\infty} dt \, \|D(X_i)\| . \qquad (10)$$

$D(X_i)$ is the deviation vector in the Schrödinger equation corresponding to the trial wave function X_i. Furthermore, if the trial wave functions are both expressible in terms of the same basis functions[21] and one requires that the Schrödinger equation be satisfied in the space subtended by the basis set, it can be shown that the integral R vanishes and $\beta = 1$; note that in this case one need not explicitly determine the second trial function X_{nR}, and the trial amplitudes C_{ni} associated with the trial wave function X_i are, according to this variational principle, second-order accurate. A second-order bound in the error term Δ has also been obtained[15]:

$$\Delta_2 = \int_{-\infty}^{\infty} dt \int_t^{\infty} dt' \, \|D(X_{nR}(t'))\| \, \|D(X_i(t))\| . \qquad (11)$$

Spruch obtained this bound on the second-order error term in a different variational principle some time ago.[14] Note that according to Eq. (8) the second-order bound Δ_2 bounds the *error in each approximate amplitude*, while the error function Δ_1 bounds *the errors in the approximate amplitudes uniformly*. Obviously it will be difficult to calculate the second-order bound Δ_2; however, in the special case of symmetric transitions, such as 1s charge exchange,[15]

$$\Delta_2 = \tfrac{1}{2}\Delta_1^2. \qquad (12)$$

In order to use Eq. (8) one must generate trial wave functions. One method is suggested by the Euler-Lagrange procedure in which one requires that[6]

$$\delta I(X_i) = \delta\left(\int_{-\infty}^{\infty} dt \, \langle X_i | H - i\frac{\partial}{\partial t} | X_i \rangle \right) = 0. \qquad (13)$$

However, if one calculates the variation in the functional I about the exact wave functions, one finds that, instead,

$$\delta I(\psi_i) = -i \sum_n A_{ni}^*(C_{ni} - A_{ni}), \qquad (14)$$

which is a first-order error. This result might, therefore, lead one to conclude that one cannot obtain a trial wave function from this procedure that differs from the exact wave function by a second-order term. However, if both trial wave functions X_{nR} and X_i obtained by this method are expressible in terms of the same basis functions, then one can demonstrate that the Euler-Lagrange method yields, *according to Eq. (8)*, second-order accurate transition amplitudes. In fact there are many methods that can be used to obtain trial wave functions: the Dirac-Frenkel methods given by Chang and Rapp[12] and Storm,[10] or the method given by Shakeshaft and Spruch[22] based on the functional considered by Demkov.[19] Logically one could also simply pick trial wave functions by trial and error, or determine parameters in a trial wave function that is required to satisfy the "familiar coupled equations" by minimizing the molecular energy. As long as the integral R vanishes, all methods yield *according to Eq. (8)* second-order-accurate transition amplitudes, and the errors in the approximate amplitudes are bounded *uniformly* by the error function. Clearly then, the error function provides a logical measure of the error associated with a particular trial wave function; other measures undoubtedly exist, but the magnitude of the error function provides a convenient common yardstick. As we will demonstrate the error function is also a valuable aid in adjusting parameters in the bounds bracketing the exact amplitudes.

The above theory rests in a fundamental manner on the assumption that the states of the unperturbed system are known, and the trial wave function belongs to the class of functions that have the same asymptotic forms as the exact wave function as $|t| \to \infty$. This is necessary since one must be able to define transition amplitudes. *This condition is not very restrictive*, and it does not rule out the possibility that the trial wave function may contain pseudostate or Sturmian functions. As long as the trial wave function belongs to the class of acceptable trial wave functions, one will be able to define approximate transition amplitudes,[5] and obtain Eq. (8). If the trial wave function does not satisfy this restriction, then one cannot define physically acceptable amplitudes, and the calculation would certainly have limited significance.

However, in the case of more complicated ion-atom collisions, one does not have the exact wave functions for the unperturbed states, and, consequently, one must introduce additional approximations. One way of dealing with this problem is to recognize that many approximate wave functions for the states of the unperturbed ion or atom are good representations of the exact states for most physical considerations. This implies that one should modify the model Hamiltonian so that it corresponds to the approximate unperturbed states at hand. For example, given a finite set of approximate wave functions one could diagonalize the Hamiltonian in this set and thereby redefine the possible unperturbed states and energy levels for the model system. The theory developed for the proton–hydrogen-atom case would then apply for transitions between these new "unperturbed states." Alternatively one could construct model Hamiltonians that contain pseudopotentials. The parameters in the pseudopotentials would be chosen such that the approximate wave functions for the unperturbed states are good representations of the outer atomlike orbitals.[23,24] In either approach, matrix elements between orbitals in the same center will vanish in the limit $|t| \to \infty$, and consequently one will be able to define impact-parameter model transition amplitudes and obtain Eq. (8).

III. CALCULATIONAL DETAILS

We consider a two-state trial wave function with the form

$$X_{1s} = (1/\sqrt{2}\,)(X^{+}_{1s} + X^{-}_{1s}), \tag{15}$$

where

$$X^{\pm}_{1s} = C^{\pm}_{1s}(t)\,\chi^{\pm}_{1s}, \tag{16}$$

and where the basis functions $\chi^{\pm}_{1s}$ are traveling 1s hydrogenlike orbitals containing the variable-charge parameters $Z^{\pm}_{s}$ and $Z^{\pm}_{p}$ and the polarization parameters $\sigma^{\pm}$:

$$\begin{aligned}\chi^{\pm}_{1s}(Z^{\pm}_{s}, Z^{\pm}_{p}, \sigma^{\pm}) = (1/\sqrt{2}\,)\{&[\Phi_{1s1}(Z^{\pm}_{s}) \pm \sigma^{\pm}\Phi_{2p_01}(Z^{\pm}_{p})] \\ &\pm [\Phi_{1s2}(Z^{\pm}_{s}) \mp \sigma^{\pm}\Phi_{2p_02}(Z^{\pm}_{p})]\} \\ = \Phi^{\pm}_{1s}(Z_{s}) \pm \sigma^{\pm}&\Phi^{\mp}_{2p_0}(Z^{\pm}_{p}).\end{aligned} \tag{17}$$

Following Bates and McCarroll[1] we choose the traveling hydrogenlike orbitals to be

$$\begin{aligned}\Phi_{1sk} &= \phi_{1s}(\vec{r}_k)e^{\pm ivz/2}e^{-i(\epsilon^{\pm}_{1s} + v^2/8)t}, \\ \Phi_{2p_0k} &= \phi_{2p_0}(\vec{r}_k)e^{\pm ivz/2}e^{-i(\epsilon^{\pm}_{1s} + v^2/8)t},\end{aligned} \tag{18}$$

where

$$\epsilon^{\pm}_{1s} = -\tfrac{1}{2}Z^{\pm 2}_{s},$$

and where $\phi_{1s}(\vec{r}_k)$ and $\phi_{2p_0}(\vec{r}_k)$ are normalized hydrogenlike orbitals centered on proton k; the upper sign in Eq. (18) applies when $k=1$, while the lower sign applies when $k=2$. Following Wilets and Gallaher,[2] the basis functions $\chi^{\pm}_{1s}$ have been chosen to have the parity ± when the electronic coordinates are reflected through the origin of the stationary coordinate system. For any set of parameters $Z^{\pm}_{s}$, $Z^{\pm}_{p}$, and $\sigma^{\pm}$, the expansion coefficients can be determined by solving the usual coupled equations which in this case is simply

$$\begin{aligned}i\frac{d}{dt}C^{\pm}_{1s} &= \frac{\langle\chi^{\pm}_{1s}|H - i\,\partial/\partial t\,|\chi^{\pm}_{1s}\rangle}{\langle\chi^{\pm}_{1s}|\chi^{\pm}_{1s}\rangle}C^{\pm}_{1s} \\ &= (G^{\pm}/S^{\pm})C^{\pm}_{1s}.\end{aligned} \tag{19}$$

The calculation of the matrix elements in Eq. (19) presents no difficulty. All single-centered integrals can be evaluated analytically. By following McCarroll,[25] the two-centered integrals can be reduced to one-dimensional integrals that can be efficiently evaluated using a Gauss-Laguerre quadrature.[26] The details of the solution of the familiar coupled equations for the expansion coefficients $C^{\pm}_{1s}$ are well known and need not be repeated here.[26]

In one series of calculations the polarization parameter was zero, and the parameters $Z^{\pm}_{s}$ were chosen to be either the static parameters given by Dalgarno and Poots,[27] the Euler-Lagrange parameters given by McCarroll, Piacentini, and Salin[8] for an energy of 2 keV and an impact parameter of $0.26a_0$, or arbitrary functions. For our work we fitted analytic functions of internuclear distance to the parameters of Dalgarno and Poots, and McCarroll, Piacentini, and Salin, and the functions are shown in Fig. 1. The Euler-Lagrange parameters of McCarroll, Piacentini, and Salin[8] and the arbitrary functions are of course dependent upon energy and impact parameter. In another series of calculations, the polarization parameters $\sigma^{\pm}$ were determined by solving the Euler-Lagrange equation. For the case of fixed functional forms for the charge parameters, the Euler-Lagrange equations for the linear expansion coefficients $C^{\pm}_{1s}$ and the polarization parameters decouple, yielding the familiar coupled equations for the $C^{\pm}_{1s}$ and simple quadratic equations for the polarization parameters. It is of interest to note the asymptotic form of the polar-

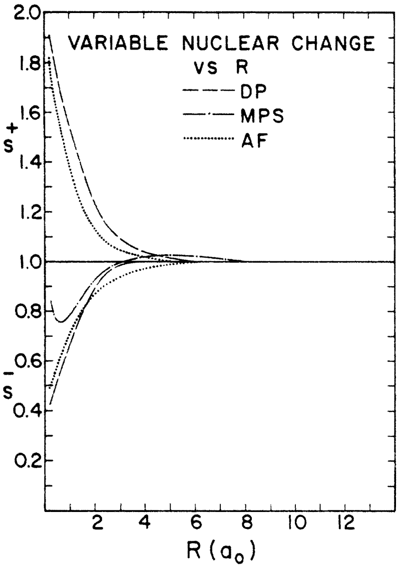

FIG. 1. Nuclear charge parameters $Z_s^\pm$ vs internuclear distance R. The curve labeled MPS[8] is based on the Euler-Lagrange method at 2 keV and an impact parameter of $0.26a_0$. The curve marked DP (Ref. 25) is based on a static molecular treatment of H_2^+. Curve AF is an arbitrary function chosen to give good values of the error function Δ_1 at 2 keV. The MPS and DP curves for $Z_s^\pm$ are nearly identical at 2 keV.

ization parameter; we find as $|t| \to \infty$

$$\sigma^\pm \sim \pm \frac{128\sqrt{2}\,(Z_p^\pm)^{5/2}}{(2+Z_p^\pm)^5[\frac{1}{4}Z_p^\pm(Z_p^\pm-1)+\epsilon_{2p}^\pm-\epsilon_{1s}^\pm]}\,\frac{1}{R^2}\,. \tag{20}$$

In one series of calculations, all the parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$ were determined by minimizing the molecular energy. We are indebted to Dr. David Dinwiddie of our laboratory,[28] who solved the static variational problem numerically for the parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$. Although this problem had been originally set up by Dickinson[29] in 1933, it was never actually solved to our knowledge. The values of the H_2^+ molecular energies are compared to

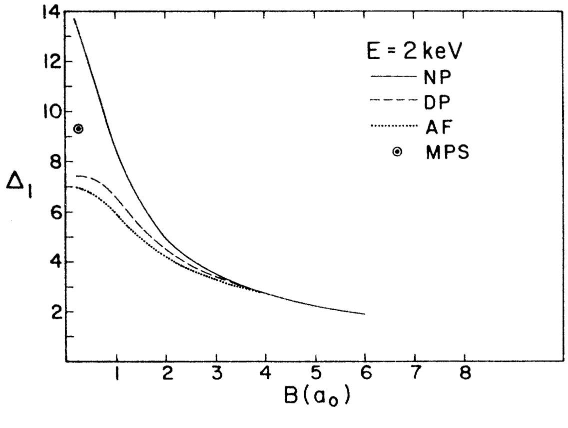

FIG. 2. Error function Δ_1 vs impact parameter at 2 keV for trial wave functions containing only the nuclear charge parameters $Z_s^\pm$, with $\sigma^\pm = 0$. Curve NP corresponds to "no parameters" with $Z_s^\pm$ set equal to unity at all R. Curves DP and AF correspond to the functions given in Fig. 1.

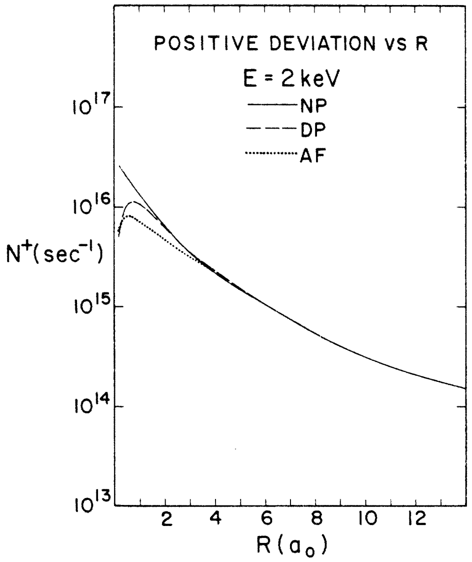

FIG. 3. Deviations for positive parity $N^+ = \|D^+\|/\hbar$ as functions of internuclear separation R at 2 keV and $B = 0.2a_0$. The curves labeled MPS, DP, and AF refer to the use of Z_s curves given in Fig. 1. The MPS and DP curves are essentially equivalent.

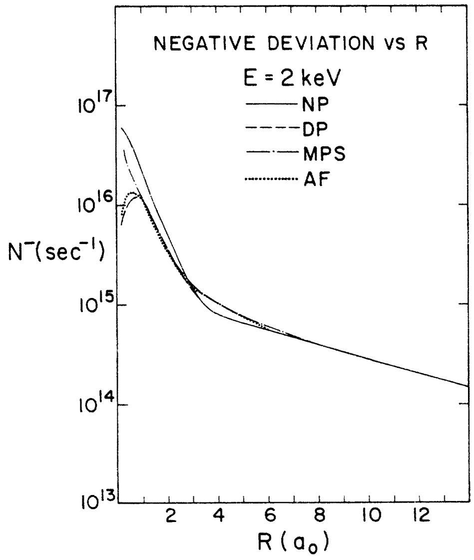

FIG. 4. Deviations for negative parity $N^- = \|D^-\|/\hbar$ as functions of internuclear separation R at 2 keV and $B = 0.2a_0$. The curves labeled MPS, DP, and AF refer to the use of Z_s^- curves given in Fig. 1.

TABLE I. Comparison of exact and approximate electronic energies of H_2^+. The approximate values were calculated by Dinwiddie (Ref. 28) using a molecular wave function given by Eq. (17), with translational factors set equal to unity.

	Σ_g		Σ_u	
$R(a_0)$	Exact	Approximate	Exact	Approximate
0.25	2.101 45	2.102 30	3.495 81	3.569 04
0.50	0.265 01	0.266 17	1.483 12	1.523 32
0.75	−0.249 05	−0.247 36	0.795 60	0.818 11
1.00	−0.451 79	−0.449 68	0.435 19	0.447 14
1.25	−0.541 80	−0.539 49	0.205 43	0.211 27
1.50	−0.582 32	−0.579 97	0.043 50	0.046 52
1.75	−0.598 72	−0.596 36	−0.076 45	−0.074 81
2.00	−0.602 64	−0.600 29	−0.167 54	−0.166 59
2.25	−0.599 95	−0.597 63	−0.237 64	−0.237 06
2.50	−0.593 82	−0.591 55	−0.292 07	−0.291 74
2.75	−0.586 02	−0.583 85	−0.334 63	−0.334 42
3.00	−0.577 56	−0.575 55	−0.368 09	−0.367 94
3.50	−0.560 86	−0.559 26	−0.415 50	−0.415 41
4.00	−0.546 09	−0.544 89	−0.445 55	−0.445 49
4.50	−0.533 94	−0.533 04	−0.464 83	−0.464 79
5.00	−0.524 42	−0.523 70	−0.477 29	−0.477 25
5.50	−0.517 23	−0.516 64	−0.485 38	−0.485 35
6.00	−0.511 97	−0.511 48	−0.490 64	−0.490 61
6.50	−0.508 21	−0.507 82	−0.494 06	−0.494 03
7.00	−0.505 59	−0.505 28	−0.496 27	−0.496 25
8.00	−0.502 57	−0.502 39	−0.498 61	−0.498 59
9.00	−0.501 19	−0.501 09	−0.499 54	−0.499 53
10.00	−0.500 58	−0.500 52	−0.499 90	−0.499 89
12.00	−0.500 17	−0.500 15	−0.500 06	−0.500 05
14.00	−0.500 07	−0.500 06	−0.500 05	−0.500 05
16.00	−0.500 03	−0.500 03	−0.500 03	−0.500 03
18.00	−0.500 02	−0.500 02	−0.500 02	−0.500 02
20.00	−0.500 02	−0.500 01	−0.500 02	−0.500 01

the exact values in Table I. It should be noted that although approximate molecular orbitals were used as basis functions, the energy phase factor in Eq. (17) is given by Eq. (18). Hence the relative phase of the two basis functions is different from that found in molecular calculations.

For a two-state trial wave function such as X_{1s} of Eq. (31), the norm of the deviation vector can be put in an interesting form which greatly facilitates the calculation of Δ_1. We have

$$||D||^2 = \left\langle \left(H - i\frac{\partial}{\partial t}\right)X_{1s} \middle| \left(H - i\frac{\partial}{\partial t}\right)X_{1s}\right\rangle , \tag{21}$$

and noting that

$$|C_{1s}^{\pm}|^2 = \langle \chi_{1s}^{\pm}|\chi_{1s}^{\pm}\rangle^{-1} , \tag{22}$$

which follows from the normalization condition, we find that

$$||D||^2 = \tfrac{1}{2}||D^+||^2 + \tfrac{1}{2}||D^-||^2 , \tag{23}$$

where

$$||D^{\pm}||^2 = (1/S^{\pm})(GG^{\pm} - |G^{\pm}|^2/S^{\pm}), \tag{24}$$

$$GG^{\pm} = \left\langle \left(H - i\frac{\partial}{\partial t}\right)\chi_{1s}^{\pm} \middle| \left(H - i\frac{\partial}{\partial t}\right)\chi_{1s}^{\pm}\right\rangle . \tag{25}$$

Note that in this special case one need not determine the linear expansion coefficients $C_{1s}^{\pm}$ in order to calculate the error function. By the straightforward application of the analysis leading from Eq. (38) to Eqs. (40)–(43) one can reduce the GG elements to a sum of matrix elements of the form

$$\langle \Phi_{jk}| f(\vec{r}_k \text{ or } \vec{r}_{k'})|\Phi_{jk'}\rangle, \quad j,j'=1s,2p, \quad k,k'=1,2 , \tag{26}$$

where $f(\vec{r}')$ is a rational function of $\vec{r}'$. All single-centered matrix elements can again be evaluated analytically, and most of the two-centered matrix elements can again be reduced to one-dimensional integrals which can be efficiently evaluated using a Gauss-Laguerre quadrature. However, the procedure cannot be applied to the matrix elements with the form

$$\langle \Phi_{j1}|r_1^{-2}|\Phi_{j2}\rangle , \tag{27}$$

which occur when $Z_s^{\pm} \neq 1$ and $Z_p^{\pm} \neq 1$. The four matrix elements of this type were reduced to two-dimensional integrals which were evaluated using Gauss-Legendre and Gauss-Laguerre quadratures. This method is not very efficient; typically the first 20 points out of a 400-point Gauss-Laguerre and a 16-point Gauss-Legendre quadratures were required. The calculation of these four integrals was the most time consuming step in the calculation. In the case of a varying $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$, the calculation for six impact parameters required approximately 35 min of CPU time on an IBM 370-155 computer, and the evaluation of these four two-dimensional integrals accounted for approximately 85% of this time.

It is of interest to note the asymptotic form of the norm of the deviation vector; using the asymptotic forms of the integrals in Appendix A we find, when $\sigma^\pm = 0$,[30]

$$||D|| \sim 1/R^2 + O(1/R^4)\,; \tag{28}$$

while using Eq. (20) for the asymptotic form of $\sigma^\pm$ we find

$$||D|| \sim \beta_1/R^2 + \beta_2/R^3 + \beta_3/R^4 + O(1/R^5)\,, \tag{29}$$

where

$$\beta_1 = \{1 + (A^2/\Omega_{31}^2)[\tfrac{1}{12} Z_p^2 (Z_p - 1)^2 + W_{31}^2 + \tfrac{1}{2} Z_p (Z_p - 1) W_{31}] - \tfrac{1}{4}(A^2/\Omega_{31})(2 + Z_p)(Z_p - 1) - 2(A^2/\Omega_{31}) W_{31}\}^{1/2}\,, \tag{30}$$

$$\beta_2 = (1/2\beta_1)\{3(A^2/\Omega_{31}) - (A^2/\Omega_{31}^2)[\tfrac{1}{2} Z_p (Z_p - 1) + W_{31}]\}^{1/2}\,, \tag{31}$$

$$\beta_3 = (1/2\beta_1)[\tfrac{9}{2} + (4A^2/\Omega_{31}^2)] - \beta_2^2/2\beta_1\,, \tag{32}$$

where we have used the fact that in the asymptotic region $Z_s^\pm = 1$ and $Z_p^\pm = Z_p$, and we define

$$A = 128\sqrt{2}\, Z_p^{5/2}/(2 + Z_p)^5\,, \tag{33}$$

$$\Omega_{31} = \tfrac{1}{4} Z_p (Z_p - 1) + W_{31}\,, \tag{34}$$

$$W_{31} = \epsilon_{2p} - \epsilon_{1s}\,. \tag{35}$$

The integral for the error function can be written as

$$\Delta_1 = 2\int_0^\infty ||D||\, dt = 2\int_0^T ||D||\, dt + 2\int_T^\infty ||D||\, dt\,, \tag{36}$$

where T is a large time ($\sim 40a_0/v$), and the first step follows from the time-reversal invariance of the matrix elements. The first integral in Eq. (36) was evaluated numerically using a standard spline integration procedure. The smaller second integral in Eq. (36) was evaluated analytically using the asymptotic forms given in Eq. (29)–(35).

IV. RESULTS AND DISCUSSION

The effect of nuclear charge parameters $Z_s^\pm$ in the basis orbitals was studied in the first series of calculations by setting the polarization parameters equal to zero. Values of the error function Δ_1 are illustrated in Fig. 2 for a range of impact parameters and an energy of 2 keV. The solid curve labeled NP corresponds to a calculation in which $Z_s^\pm = 1$; or just the two-state traveling hydrogenic calculation of McCarroll.[25] The dashed curve labeled DP corresponds to a calculation in which the static charge parameters shown in Fig. 1 were used, while the dot labeled MPS corresponds to the calculation in which the Euler-Lagrange parameters shown in Fig. 1 were used. The dotted curve labeled AF corresponds to the calculation in which the judiciously chosen but, nevertheless, arbitrary functions shown in Fig. 1 were used as the charge parameters.

As discussed in Sec. II, the error function provides according to Eq. (8) a common measure to assess the error associated with each trial wave function. The fact that the error function is smaller in the static case indicates that by this measure the Euler-Lagrange variational method is not superior to the static method. The fact that one can choose arbitrary functions as charge parameters and obtain values of Δ_1 lower than those obtained in either the static or Euler-Lagrange cases indicates that by this measure, neither the static nor the dynamic Euler-Lagrange variational methods is the optimum method.

It is also possible to analyze the norm of the deviation vector during the collision. The parity components $||D^\pm||$ are shown in Figs. 3 and 4 for these three calculations. A study of Figs. 3 and 4 indicates that the superiority of the static method to the Euler-Lagrange method in this case can be largely attributed to the fact that the error function $||D^-||$ increases at internuclear separations less than $R = 0.75$ where the parameter Z_s^- turns upward. This conclusion is in conflict with the argument given by Cheshire that would lead one to expect that Z_s^- should approach unity as $R \to 0$.[6] It should be noted that Cheshire's argument[6] is based on the assumption that the translational factors introduced by Bates and McCarroll[1] are correct at small internuclear separations, and it seems unlikely that this assumption is valid.[31] Finally, it is of interest to note that the arbitrary functions used as charge parameters in the calculation labeled AF were chosen by analyzing the parity error functions for a variety of functions. Such a trial and error approach may have merit in general, since it appears to be time consuming to determine parameters by solving the necessary equations.

In the second series of calculations the effect of the polarization parameters $\sigma^\pm$ was investigated. The variable-charge parameters $Z_s^\pm$ were set

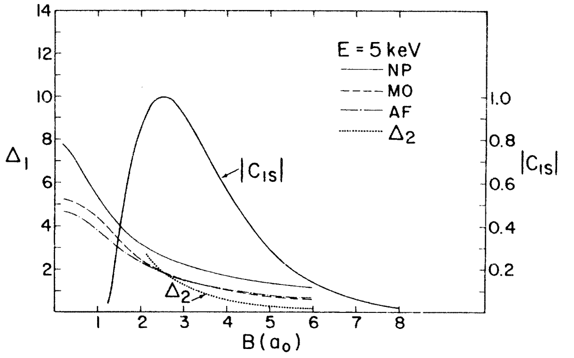

FIG. 5. Error function Δ_1 and 1*s* charge-exchange amplitude $|C_{1s}|$ vs impact parameter B at 5 keV for trial wave functions containing all six parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$. Symbols are the same as in Figs. 1 and 2. The error function $\Delta_2 = \frac{1}{2}\Delta_1^2$ is also plotted for curve MO, which refers to Dinwiddie's approximate molecular parameters.

equal to unity, and the charge parameters $Z_p^\pm$ were taken to be either one or two. The results obtained in these calculations indicate that choosing $Z_p^\pm = 2$ is superior to choosing $Z_p^\pm = 1$, and again it appears that the static method is superior to the Euler-Lagrange method.

In the final series of calculations, all the parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$ were allowed to vary during the collision, and values of the error function are shown in Fig. 5 for an energy of 5 keV. The curve labeled NP again corresponds to the two-state traveling hydrogenic calculation with no adjustable parameters included, and the curve labeled MO corresponds to a calculation in which the static parameters were used. The curve labeled AF again corresponds to a calculation in which a set of arbitrary functions were used as parameters, and these arbitrary functions were chosen by analyzing the deviation curves $||D^\pm||$ for a variety of arbitrary functions. The solid oscillatory curve corresponds to the approximate 1*s* charge-exchange amplitudes obtained when the molecularlike orbitals were used as basis orbitals. Finally, the dotted curve Δ_2 shows values of the second-order error bound Δ_2 for the molecular-type trial wave function, and, as shown in Table II, the magnitudes of the second-order bound are only slightly larger than those of the approximate 1*s* charge-exchange amplitudes for the range of impact parameters 3.5–6.0. In view of the simplicity of the trial wave function we consider this to be an encouraging result, and we feel that there is hope that a more sophisticated trial wave function will result in lower bounds.

TABLE II. Comparison of approximate 1*s* charge-exchange amplitudes $|C_{1s}|$ with values of the second-order bound Δ_2 for an energy of 5 keV.

$B(a_0)$	$\|C_{1s}\|$	Δ_2
3.5	0.75	0.85
4.0	0.57	0.60
4.5	0.41	0.41
5.0	0.29	0.31
5.5	0.21	0.25
6.0	0.14	0.20

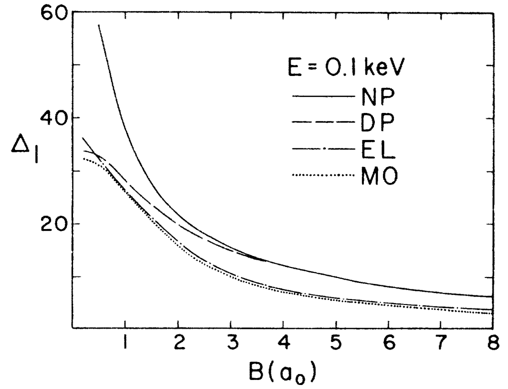

FIG. 6. Error function Δ_1 as a function of impact parameter B at 0.1 keV for trial functions containing all six parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$. The symbol NP refers to the case where $Z_s^\pm = 1$ and $\sigma^\pm = 0$. The symbol EL corresponds to an Euler-Lagrange calculation of these parameters, and DP refers to Dalgarno and Poots's molecular calculations of the parameters. MO refers to use of Dinwiddie's approximate molecular parameters.

In Figs. 6–10 the values of the error function obtained by employing parameters from the NP case, the DP case, the Euler-Lagrange polarization calculation, and the molecular-type calcula-

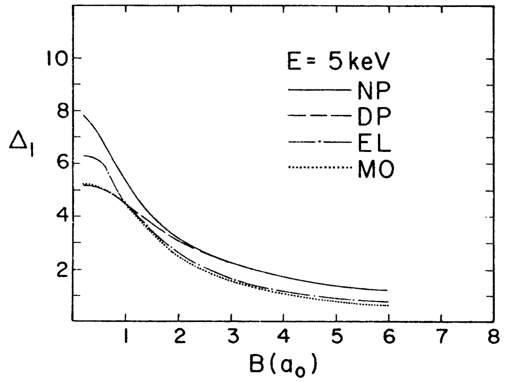

FIG. 7. Error function Δ_1 as a function of impact parameter B at 5 keV for trial functions containing all six parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$. The symbol NP refers to the case where $Z_s^\pm = 1$ and $\sigma^\pm = 0$. The symbol EL corresponds to an Euler-Lagrange calculation of these parameters, and DP refers to Dalgarno and Poots's molecular calculations of the parameters. MO refers to use of Dinwiddie's approximate molecular parameters.

tion are compared at various energies. At an energy of 25 keV the velocity of the incident proton is approximately that of an electron in the first Bohr orbit, and, hence, it is not surprising that the molecular-type trial wave function is superior to the atomic-type trial wave function for energies below 25 keV, while the reverse is true for energies greater than 25 keV. It may be somewhat surprising, however, to observe that the trial wave function with the Euler-Lagrange polarization parameters yields bounds in the 100-keV case that are inferior to those obtained with just the traveling 1*s* hydrogenic trial wave function. Figures 6–10 indicate that it is important to account for the polarization of the atom. In fact, except for impact parameters less than ~$1a_0$, it appears that polarization is more effective than variable nuclear charge in reducing calculated bounds.

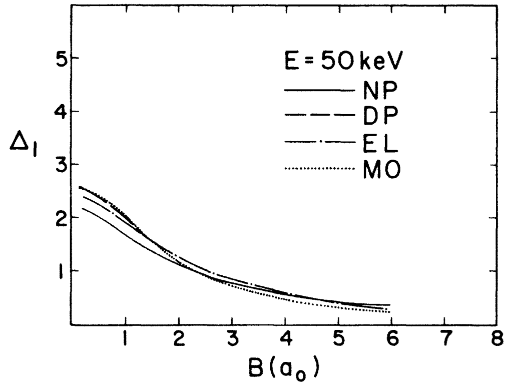

FIG. 9. Error function Δ_1 as a function of impact parameter *B* at 50 keV for trial functions containing all six parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$. The symbol NP refers to the case where $Z_s^\pm = 1$ and $\sigma^\pm = 0$. The symbol EL corresponds to an Euler-Lagrange calculation of these parameters, and DP refers to Dalgarno and Poots's molecular calculations of the parameters. MO refers to use of Dinwiddie's approximate molecular parameters.

It is perhaps of interest at this point to consider ways in which the error function might be reduced in future work. First consider the results shown in Fig. 4 for 5 keV. At an impact parameter of $4a_0$, where the approximate charge-exchange amplitude is roughly 0.5, we note from the asymptotic form of the norm of the deviation vector shown in Eq. (28) that roughly 40% of the error associated with the two-state traveling hydrogenic trial wave function can be attributed to the integration of the $1/R^2$ term in Eq. (28) from $R = \mp\infty$ to $R = \mp 10a_0$. The account of the polarization of the atom provided by the polarized 1*s* functions used in this work modifies the asymptotic form of the deviation vector as shown in Eq. (29) and thereby reduces the error by approximately 40%. However, if one considers the asymptotic form of the norm of the deviation vector given by Shakeshaft[32] for the case of exact H_2^+ molecular basis orbitals, it is observed that the $1/R^2$ term does not occur, reflecting the fact that the exact H_2^+ traveling molecular basis functions provide a better account of the long-range polarization effect. It may, therefore, be possible to obtain a reduction in the magnitude of the second-order bound by using 1*s* hydrogenlike orbitals that provide a more sophisticated account of polarization. First, one could parametrize the *p*-like character in the 1*s* orbitals in a way that would allow the direction of

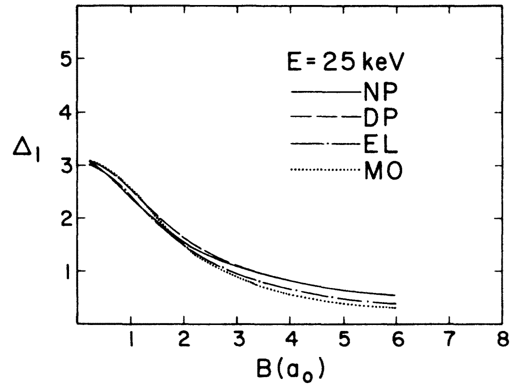

FIG. 8. Error function Δ_1 as a function of impact parameter *B* at 25 keV for trial functions containing all six parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$. The symbol NP refers to the case where $Z_s^\pm = 1$ and $\sigma^\pm = 0$. The symbol EL corresponds to an Euler-Lagrange calculation of these parameters, and DP refers to Dalgarno and Poots's molecular calculations of the parameters. MO refers to use of Dinwiddie's approximate molecular parameters.

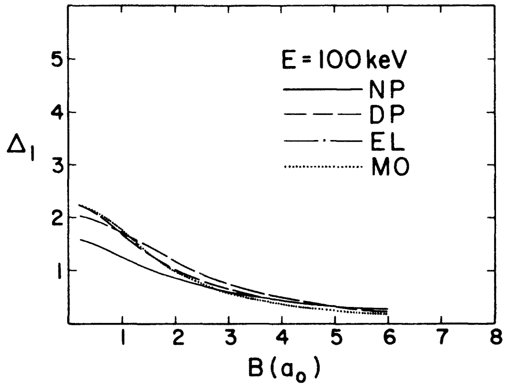

FIG. 10. Error function Δ_1 as a function of impact parameter *B* at 100 keV for trial functions containing all six parameters $Z_s^\pm$, $Z_p^\pm$, and $\sigma^\pm$. The symbol NP refers to the case where $Z_s^\pm = 1$ and $\sigma^\pm = 0$. The symbol EL corresponds to an Euler-Lagrange calculation of these parameters, and DP refers to Dalgarno and Poots's molecular calculations of the parameters. MO refers to use of Dinwiddie's approximate molecular parameters.

polarization to lag the $R(t)$ direction; this dynamic effect is partly responsible for the π coupling in molecular calculations. Second, one observes that the essential difference between the approximate H_2^+ molecular-type basis functions used in this work and exact H_2^+ molecular basis functions is really a difference in the phase factors in the two types of basis functions; this suggests that it might be possible to obtain an improvement by including parameters in the "energy phase factors," and then choose these factors to minimize the norm of the deviation vector in the asymptotic region.

It would also be of interest to investigate the suggestion of Schniederman and Russek[31] that one include parameters in the traveling or translational factors in the basis functions. The effect of such parameters could easily be studied in the two-state calculation described here, using the magnitude of the norm of the deviation vector as a guide in choosing suitable functions for the parameter $f(\vec{r},\vec{R})$ suggested by Schniederman and Russek.[31]

Finally, one might expect that the error function could be reduced by including more states, possibly parametrized, in the trial wave function. Rather extensive calculations have been reported[2-4,26] with as many as seven states on each proton included in the trial wave function.[26] The excited states affect the 1s charge-exchange amplitudes somewhat, and it seems likely that the addition of these excited states would reduce the error.

One might be concerned that such work might be limited in accuracy since the trial functions do not account for the ionization process.[32] We note that the cross sections for ionization are small, especially so for energies below 25 keV.[33] This suggests that the flux lost to the ionization must be small in the asymptotic region. Now continuum effects can be quite large for, say, $R<15a_0$, but it is possible in principle to completely account for the continuum in a finite region of space with square-integrable functions. Viewed generally, the indirect variational approach provides a framework in which to do this; one includes parameters in square-integral basis functions and then chooses the parameters to minimize the error function. In fact, if it should become difficult to choose parameters on the basis of physical intuition, it might be useful to choose a trial wave function that consists of two parts; one part would contain the approximate amplitudes and would take the proper form as $|t|\rightarrow\infty$; the other part would vanish in the asymptotic regions but would contain arbitrary parameters that would be chosen to minimize the error for $R<15a_0$.

APPENDIX A

As observed by Aspinall and Percival,[34] it is possible to evaluate analytically matrix elements of the form

$$CC_{jj}=\langle\Phi_{j1}|r_2^{-2}|\Phi_{j1}\rangle\,. \tag{A1}$$

Specifically we find

$$CC_{ss}=2(Z_s)^2[K_1+(1/2Z_s^{\pm})K_0]\,, \tag{A2}$$

$$\begin{aligned}CC_{pp}=-\frac{(Z_p)^5}{32R^2}\biggl(&\frac{24}{Z_p^5}+\frac{2R^2}{Z_p^3}-\frac{1}{Z_p}K_5-\frac{5}{Z_p^2}K_4-2\;\frac{10+Z_p^2R^2}{Z_p^3}\;K_3\\&-6\;\frac{10+Z_p^2R^2}{Z_p^4}\;K_2-\frac{12(10+Z_p^2R^2)+Z_p^4R^4}{Z_p^5}\;K_1-\frac{12(10+Z_p^2R^2)+Z_p^4R^4}{Z_p^6}\,K_0\biggr)\,,\end{aligned} \tag{A3}$$

$$CC_{ps}=-\frac{(Z_s)^{3/2}(Z_p)^{5/2}}{2\sqrt{2}\,R}\left(\frac{2}{\gamma}-\frac{1}{\gamma}K_3-\frac{3}{\gamma^2}K_2+\frac{6+\gamma^2R^2}{\gamma^3}\;K_1-\frac{6+\gamma^2R^2}{\gamma^4}K_0\right)\,, \tag{A4}$$

where Z_s and Z_p are the charge parameters in the orbitals, and

$$\gamma=Z_s+\tfrac{1}{2}Z_p\,, \tag{A5}$$

$$K_{2n}=\tfrac{1}{2}R^{2n-1}[e^{-\alpha R}E_i(\alpha R)-e^{\alpha R}E_i(-\alpha R)]-\frac{1}{\alpha^{2n-1}}\sum_{k=1}^{n}(2n-2k)!\,(\alpha R)^{2k-2}\,, \tag{A6}$$

$$K_{2n+1}=\tfrac{1}{2}R^{2n}[e^{\alpha R}E_i(-\alpha R)+e^{-\alpha R}E_i(\alpha R)]-\frac{1}{\alpha^{2n}}\sum_{k=1}^{n}(2n-2k+1)!\,(\alpha R)^{2k-2}\,, \tag{A7}$$

where $E_i(\alpha R)$ is the exponential integral[35] and α represents either Z_s, Z_p, or γ. From the asymptotic expansion[35] for the exponential integral, we find from Eqs. (A2)–(A7) that as $R\rightarrow\infty$

$$CC_{ss}\sim\frac{1}{R^2}+\frac{1}{R^4}+\frac{9}{2}\;\frac{1}{R^6}+\cdots\,, \tag{A8}$$

$$CC_{pp}\sim\frac{2\sqrt{2}}{R}\;\frac{(Z_p)^{5/2}}{(2+Z_p)^3}\;\frac{32}{(Z_pR)^2}+\frac{384}{(Z_pR)^4}+\frac{864}{(Z_pR)^6}+\cdots\,, \tag{A9}$$

$$CC_{ps} \sim \frac{256\sqrt{2}\, Z_p^{5/2}}{(2+Z_p)^5}\, \frac{1}{R^3} + \frac{12\,288\sqrt{2}\, (Z_p)^{5/2}}{(2+Z_p)^7}\, \frac{1}{R^4} + \cdots , \tag{A10}$$

which are needed to derive the asymptotic forms of the norm of the deviation vector given in Eqs. (28)-(35).

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