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Theory of Proton–Hydrogen Collisions

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The theory of excitation and charge exchange in proton-hydrogen collisions is discussed within the framework of the impact-parameter method. Consideration is given to the importance of proper boundary conditions. The time-dependent equations linking the amplitudes of the target with those of the rearranged system are written in matrix form. By eliminating the rearrangement amplitudes from these equations, a second-order matrix equation is derived which may be used as a basis for successive approximations which are automatically second order. The theory is generalized with the aid of a two-center expansion of the electronic wave function. The method is illustrated by computing first- and second-order distortion approximations for the reactions $H^++H(1s) \rightarrow H^++H(2s)$ and $H^++H(1s) \rightarrow H(1s)+H^+$, and the results are compared with previous calculations.

I. INTRODUCTION

IN this paper we shall be concerned with methods of calculating the excitation and charge-exchange cross sections of proton-hydrogen collisions. Our interest will lie mainly in the kilovolt region and for this purpose it is sufficient to use the well-known "impact-parameter method"[1] (IPM) in which the protons are treated as classical particles moving with constant relative velocity. Thus only the electron need be treated quantum mechanically as it moves in the time-dependent field of the "infinitely massive" protons.

Unfortunately, the apparent simplicity of this problem is plagued by the usual bugbear of atomic-scattering theory; the necessity of accounting for the infinite number of hydrogenic states. Specifically, the strong coupling found in calculations based on expansions in atomic orbitals seems to indicate a strong coupling with states excluded from the calculation and the subsequent slow convergence of this approach.[2] This difficulty is somewhat aggravated by the fact that virtually all inelastic channels are energetically permissible. However, relatively little is known about this coupling and detailed investigations are only now being made.[3] At high energies recent studies indicate that the influence of the continuum may well be decisive.[4] Moreover, since it is not clear how this latter effect could be incorporated in the usual expansion methods, it is possible that these methods may converge to an incorrect result. In order to investigate this possibility we have devised an approximation scheme based on an expansion in atomic orbitals but which simultaneously includes an effect from all those states (including the continuum) which have not been explicitly included in the calculation. Thus, to parallel the usual "first-order methods" we derive a set of "second-order methods."

A partial review of first-order methods is given in Sec. III using a matrix notation introduced in Sec. II. In contrast with previous authors[5] we place particular emphasis on the importance of correct boundary conditions. For resonant charge transfer we introduce a distortion approximation and a modification of the Brinkman-Kramers approximation both of which have the correct boundary conditions. However, the main purpose of the review is to show clearly the analogies between the first-order methods and the second-order methods introduced in Sec. IV and to present the matrix equations necessary in the derivation of these second-order methods. Finally, in Sec. V, we calculate cross sections for the reactions

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

and

$$H^++H(1S) \rightarrow H^++H(2S),$$

according to the distortion approximation in both the first- and second-order methods, and we discuss the significance of the results.

II. NOTATION

Let e, A, and B denote the electron, the target proton, and the incident proton, respectively. Let $\mathbf{R}$ be the position vector of B relative to A and let $\mathbf{r}_A$, $\mathbf{r}_B$, and $\mathbf{r}$ be the position vectors of e relative to A, B, and the midpoint of AB. In the IPM it is assumed that A remains fixed while B moves in a straight line with a constant speed v. Thus $\mathbf{R}=\boldsymbol{\rho}+\mathbf{v}t$ where t is the time, chosen such that at $t=0$ the protons, A and B, have a minimum separation $\boldsymbol{\rho}$, which is the impact parameter for the collision.

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[1] See, for example, J. W. R. Fennema, in *Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collision* (North-Holland Publishing Company, Amsterdam, 1964). The IPM is here understood as a method of computing total cross sections and we shall not be concerned with differential cross sections. See, for example, D. R. Bates and D. A. Williams, Proc. Phys. Soc. (London) **83**, 425 (1964).

[2] T. Y. Wu and T. Ohmua, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), pp. 225.

[3] S. E. Lovell and M. B. McElroy, Space Division, Kitt Peak National Observatory, Tucson, Arizona, 1964 (to be published).

[4] I. M. Chesire, Proc. Phys. Soc. (London) **84**, 89 (1964).

[5] Previous treatments stress the importance of correcting for the lack of orthogonality between the initial and final states in charge transfer. D. R. Bates, Proc. Roy. Soc. (London) **A247**, 294 (1958); M. H. Mittleman, Phys. Rev. **122**, 499 (1961). For a more comprehensive review of the field, see D. R. Bates, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1962), p. 549.

The time-dependent Schrödinger equation (in atomic units)[6] for the complete electronic wave function $\Psi(\mathbf{r},t)$ is

$$(T_A+V_B)\Psi=0 \tag{1a}$$

or

$$(T_B+V_A)\Psi=0\,, \tag{1b}$$

where

$$T_A=\tfrac{1}{2}\nabla_r^2+1/r_A+i(\partial/\partial t)\,,\quad V_A=1/r_A\,, \tag{2a}$$

$$T_B=\tfrac{1}{2}\nabla_r^2+1/r_B+i(\partial/\partial t)\,,\quad V_B=1/r_B\,. \tag{2b}$$

If $\phi_n(\mathbf{r})$ denotes a hydrogenic eigenfunction with eigenenergy ϵ_n so that

$$(\tfrac{1}{2}\nabla^2+1/r+\epsilon_n)\phi_n(\mathbf{r})=0\,, \tag{3}$$

then

$$\Phi_n{}^A=\phi_n(\mathbf{r}_A)\exp(-i\{\tfrac{1}{2}\mathbf{v}\cdot\mathbf{r}+\tfrac{1}{8}v^2t+\epsilon_n t\}) \tag{4a}$$

$$\Phi_n{}^B=\phi_n(\mathbf{r}_B)\exp(+i\{\tfrac{1}{2}\mathbf{v}\cdot\mathbf{r}-\tfrac{1}{8}v^2t-\epsilon_n t\}) \tag{4b}$$

are exact solutions of the unperturbed equations

$$T_A\Phi_n{}^A=0\,, \tag{5a}$$

$$T_B\Phi_n{}^B=0\,, \tag{5b}$$

and form two mutually exclusive complete orthogonal sets. Consequently we may expand Ψ as

$$\Psi=\Phi^A A \tag{6a}$$

or

$$\Psi=\Phi^B B\,, \tag{6b}$$

where Φ^A and Φ^B are row matrices with elements $\Phi_n{}^A$ and $\Phi_n{}^B$, while A and B are column matrices with elements $a_n(t)$ and $b_n(t)$. The scalar products (6a), (6b) imply integration over the continuum as well as summation over all bound states.

If (1a) and (1b) are solved subject to the boundary condition[4]

$$a_n \xrightarrow[t\to-\infty]{} (vR-v^2t)^{-i/v}\delta_{np}\,, \tag{7}$$

then the probability of excitation of the target from an initial state (p) to a final state (q) is

$$P_A(p,q)=\lim_{t\to+\infty}|a_q(t)|^2 \tag{8a}$$

and the probability of charge transfer to a state (q) is

$$P_B(p,q)=\lim_{t\to+\infty}|b_q(t)|^2. \tag{8b}$$

The corresponding cross sections are obtained by integrating over all possible impact parameters

$$Q_{A,B}(p,q)=\int d\varrho P_{A,B}(p,q)\,. \tag{9}$$

III. FIRST-ORDER METHODS

By projecting the states Φ^A and Φ^B on (1a) and (1b) we obtain

$$(\Phi^A|T_A|\Psi)=-(\Phi^A|V_B|\Psi) \tag{10a}$$

$$(\Phi^B|T_B|\Psi)=-(\Phi^B|V_A|\Psi)\,, \tag{10b}$$

where

$$(\Phi_n{}^{A,B}|\mathfrak{L}|\Psi)=\int d\mathbf{r}\Phi_n{}^{A,B*}(\mathbf{r},t)\mathfrak{L}(\mathbf{r},t)\Psi(\mathbf{r},t)\,. \tag{11}$$

Equations (10a) and (10b) are entirely equivalent to (1a) and (1b) and form a convenient starting point for our discussion of first-order methods.

Substituting (6a) in (10a) and (6b) in (10b) gives

$$dA/dt=i(\Phi^A|V_B|\Phi^A)A\,, \tag{12a}$$

$$dB/dt=i(\Phi^B|V_A|\Phi^B)B\,, \tag{12b}$$

where $(\Phi^A|V_B|\Phi^A)$ and $(\Phi^B|V_A|\Phi^B)$ are square matrices whose (n,m)th elements are $(\Phi_n{}^A|V_B|\Phi_m{}^A)$ and $(\Phi_n{}^B|V_A|\Phi_m{}^B)$. Approximations to (12a) may be made by retaining only a few specific elements of $(\Phi^A|V_B|\Phi^A)$. For example, by retaining only the diagonal elements the equation is uncoupled and solved by

$$a_n=\delta_{np}\exp\left\{i\int^t(\Phi_n{}^A|V_B|\Phi_n{}^A)dt'\right\}\,, \tag{13}$$

which satisfies (7). To obtain an estimate of $a_q(q\neq p)$ we neglect all terms containing states other than (p) and (q), to give

$$\dot{a}_q=V_{qq}a_q+V_{qp}a_p\,, \tag{14}$$

where

$$V_{nm}=(\Phi_n{}^A|V_B|\Phi_m{}^B)\,. \tag{15}$$

Equation (14) is solved by[7]

$$a_q=\exp\left\{i\int^t V_{qq}dt'\right\}\int_{-\infty}^t dt'V_{qp}a_p \times\exp\left\{-i\int^{t'}V_{qq}dt''\right\}\,, \tag{16}$$

which, from (8a), leads to the excitation probability

$$P_A(p,q)\simeq\left|\int_{-\infty}^{\infty}dtV_{qp}a_p\exp\left\{-i\int^t V_{qq}dt'\right\}\right|^2. \tag{17}$$

Substituting (13) for a_p in (17) gives the well-known distortion approximation introduced by Bates[7] in his calculations of $Q_A(1s,2s)$ and $Q_A(1s,2p)$. Approximation (17) will prove useful when further methods of computing a_p are discussed later in this paper.

To proceed further with (12a) we may solve numerically the coupled equations which result when certain specific elements are retained. For example, $Q_A(1s,2s)$ has been calculated in the[3] $1sA/2sA$ and in the[8]

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[6] Atomic units will be used throughout this paper: 1 a.u. of time $=2.42.10^{-17}$ sec; 1 a.u. of energy $=27.2$ eV; 1 a.u. of length $=a_0=0.53$ Å; 1 a.u. of velocity $=2.18\times10^8$ cm/sec. It is useful to note that the energy of the incident proton in the laboratory frame of reference is $E=25\,v^2$ (keV).

[7] D. R. Bates, Proc. Phys. Soc. (London) **72**, 227 (1959); **A77**, 59 (1961).

[8] M. H. Mittleman, Phys. Rev. **129**, 190 (1963).

$1sA/2sA/2pA$ approximations to (12a). By including higher states more accurate results may be expected. However, the convergence is likely to be slow since no allowance has been made for coupling with rearrangement states. Moreover, since the boundary condition (7) is embedded in the continuum of B the usefulness of (12b) is greatly restricted[9]; indeed from a computational point of view it is virtually useless.

As an alternative to (12a) and (12b) we interchange the substitutions of (6) in the right-hand side of (10) to obtain

$$dA/dt=i(\Phi^A|V_B|\Phi^B)B\,, \tag{18a}$$

$$dB/dt=i(\Phi^B|V_A|\Phi^A)A\,. \tag{18b}$$

Clearly, if we already have a knowledge of A, (18b) may be integrated to give the charge-exchange amplitude

$$P_B(p,q)=\left|\int_{-\infty}^{\infty} dt(\Phi_q{}^B|V_A|\Phi^A)A\right|^2. \tag{19}$$

The well-known Brinkman-Kramers[10] (BK) approximation is obtained from (19) by making the substitution $a_n=\delta_{np}$. This is inconsistent with (7). Instead of δ_{np} we substitute $\delta_{np}(vR-v^2t)^{-i/v}$ for a_n in (19) to obtain a modified Brinkman-Kramers (MBK) approximation which is consistent with (7). The situation may be further improved by substituting (13) for a_n in (19) to give a distortion approximation analogous to that described above for excitation.

As a basis for successive approximations, however, (18a) and (18b) are defective. This is illustrated by considering the diagonal approximation

$$\dot{a}_n=i(\Phi_n{}^A|V_B|\Phi_n{}^B)b_n\,, \tag{20a}$$

$$\dot{b}_n=i(\Phi_n{}^B|V_A|\Phi_n{}^A)a_n\,, \tag{20b}$$

which has the general solution

$$a_n=c_1\exp i\gamma_n+c_2\exp -i\gamma_n\,, \tag{21a}$$

$$b_n=c_1\exp i\gamma_n-c_2\exp -i\gamma_n\,, \tag{21b}$$

where

$$\gamma_n=\int_{-\infty}^{t}(\Phi_n{}^B|V_B|\Phi_n{}^A)dt' =\int_{-\infty}^{t}(\Phi_n{}^A|V_A|\Phi_n{}^B)dt'\,, \tag{22}$$

and c_1 and c_2 are arbitrary constants. It is easily shown that γ_n vanishes rapidly for large negative t so that (21a) is inconsistent with (7). This fundamental discrepancy cannot be resolved by the inclusion of further bound states.

To overcome the defects of (12a) and (12b) we expand Ψ in an overcomplete set

$$\Psi=\Phi^A A+\Phi^B B, \tag{23}$$

where A and B are to be determined by (10a) and (10b). The beauty of this two-center expansion is that it makes explicit allowance for each reaction path and thus circumvents the defects of the single-center expansions (6a) and (6b) where rearrangement states are awkwardly contained in the continuum and thus confused with ionization states. Perhaps an even better expansion would result if, for example, the second term on the right-hand side of (23) were restricted to a summation over bound states only. We would then have a clearer physical interpretation for the continuum elements of A which would correspond to pure ionization. This introduces a slight complication, however, and since we are here mainly concerned with excitation and charge transfer we shall simply exploit the symmetry of (23). Clearly the bound-state coefficients of (23) must coincide with those of (6a) and (6b) at infinite proton separation and there is no need to alter the probability definitions (8a) and (8b).

Substituting (23) in (10a) and (10b) gives

$$dA/dt+(\Phi^A|\Phi^B)(dB/dt) =i(\Phi^A|V_B|\Phi^A)A+i(\Phi^A|V_A|\Phi^B)B\,, \tag{24a}$$

$$dB/dt+(\Phi^B|\Phi^A)(dA/dt) =i(\Phi^B|V_A|\Phi^B)B+i(\Phi^B|V_B|\Phi^A)A\,. \tag{24b}$$

Again it is instructive to consider the diagonal approximation. This approximation coincides with the two-state approximation of Bates[11] and has been solved by McCarroll.[12] The solution may be put in the form

$$a_n=\delta_{np}(vR-v^2t)^{-i/v}e^{i\alpha_n}\cos\beta_n\,, \tag{25a}$$

$$b_n=\delta_{np}(vR-v^2t)^{-i/v}e^{i\alpha_n}\sin\beta_n\,, \tag{25b}$$

where α_n and β_n are real and vanish as t tends to $-\infty$. The boundary condition (7) is therefore satisfied by (25a) in contrast with (21a).

IV. SECOND-ORDER METHODS

Broadly speaking, the methods discussed so far may be considered in the following way: By restricting the number of available states to a select few we obtain a tractable model which may be treated precisely by numerical methods. This is equivalent to allowing for an infinite number of transitions between a limited number of states, and it neglects completely effects due to all other inelastic processes. Thus the continuum, which may play an extremely important role in the intermediate stages of the collision, is neglected. Methods which attempt to take account of such transitions are loosely termed "second order." For example, the second Born,[13] the impulse,[14] and the continuum

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[9] Note, however, the rather elegant usage of (12b) by M. H. Mittleman, Phys. Rev. **122**, 499 (1961).

[10] H. C. Brinkman and H. A. Kramers, Proc. Acad. Sci. Amsterdam **33**, 973 (1930).

[11] D. R. Bates, Proc. Roy. Soc. (London) **A247**, 294 (1958).

[12] R. McCarroll, Proc. Roy. Soc. (London) **A264**, 547 (1961).

[13] R. M. Drisko, thesis, Carnegie Institute of Technology, 1956 (unpublished).

[14] B. H. Bransden and I. M. Cheshire, Proc. Phys. Soc. (London) **81**, 820 (1963); I. M. Cheshire, *ibid.* **82**, 113 (1963); see also R. A. Mapleton, *ibid.* **83**, 35 (1964).

distorted wave[4] approximations may be thought of in this light. The significant feature of these approximations is that, for resonant charge transfer from the $(1s)$ state, they all predict the high-energy behavior[15]

$$Q_B(1s,1s)\simeq(0.2946+\mu v)Q_B{}^{BK}(1s,1s)\,, \tag{26}$$

where μ is a small (and for our purposes, insignificant) constant, and $Q_B{}^{BK}(1s,1s)$ is the Brinkman-Kramers cross section

$$Q_B{}^{BK}(1s,1s)=\frac{256}{5v^2}(1+\tfrac{1}{4}v^2)^{-5}(\pi a_0{}^2)\,. \tag{27}$$

This is in very sharp contrast with the high-energy behavior of first-order methods. The two-state Bates-McCarroll approximation behaves like[12] $Q_B{}^{BK}(1s,1s)$ at high energies, and there is no reason to suspect that this will be significantly altered by the inclusion of further bound states. However, the second-order methods mentioned above give poor results at low energies (below 30 keV) and seem to be incapable of systematic improvement. Moreover, one's confidence in (26) is, to some extent, undermined by the likelihood that the Born series diverges for rearrangement collisions.[16] Clearly it would be advantageous to devise an approximation scheme which includes effects from all inelastic processes and which may simultaneously be treated by successive approximations based on the inclusion of the more significant discrete states. We now proceed towards this end.

First, let us consider how we could, in principle, solve the coupled equations (18a) and (18b). Suppose we start by substituting a given first-order approximation to A in (18b). We could then calculate each element of B and substitute the result in (18a). This would involve an infinite number of coefficients b_n corresponding to the infinite number of available hydrogenic states. Moreover, the most important of these (corresponding to rearrangements) are embedded in the continuum. Nevertheless, having surmounted these barriers we would now perform the infinite sum implied in the right-hand side of (18a) and proceed to calculate the second-order approximation to A. We would then repeat this process and hope that A would converge in successive iterations. However, if we could somehow eliminate B from (18a) and (18b) the intermediate stages described above would automatically be contained in the resulting equation for A. This is the central idea of the present paper. The process of eliminating B from (18a) and (18b) is now performed.

Assuming the existence of the matrix $(\Phi^B|\,V_B{}^{-1}|\Phi^A)$, we consider the product

$$\begin{aligned}(\Phi^B|\,V_B{}^{-1}|\Phi^A)(\Phi^A|\,V_B|\Phi^B)&=(\Phi^B|\,V_B{}^{-1}V_B|\Phi^B)\\&=(\Phi^B|\Phi^B)=I\,,\end{aligned} \tag{28}$$

where I denotes the unit matrix. In the derivation of (28) we have made use of the closure property of Φ^A together with the orthogonality of Φ^B. Similarly, we can show that

$$(\Phi^A|\,V_B|\Phi^B)(\Phi^B|\,V_B{}^{-1}|\Phi^A)=I\,, \tag{29}$$

so that, formally,

$$(\Phi^B|\,V_B{}^{-1}|\Phi^A)=(\Phi^A|\,V_B|\Phi^B)^{-1}\,. \tag{30}$$

This enables us to write (18a) as

$$B=-i(\Phi^B|\,V_B{}^{-1}|\Phi^A)\dot{A} \tag{31}$$

and, differentiating both sides,

$$\frac{dB}{dt}=-\left\{i\frac{d}{dt}(\Phi^B|\,V_B{}^{-1}|\Phi^A)\right\}\frac{dA}{dt}-i(\Phi^B|\,V_B{}^{-1}|\Phi^A)\frac{d^2A}{dt^2}\,. \tag{32}$$

Making use of (5b) and assuming the validity of Green's theorem, we have

$$i(d/dt)(\Phi^B|\,V_B{}^{-1}|\Phi^A)=(\Phi^B|\,T_BV_B{}^{-1}|\Phi^A)\,, \tag{33}$$

whence (32) becomes

$$i\frac{dB}{dt}=(\Phi^B|\,V_B{}^{-1}|\Phi^A)\frac{d^2A}{dt^2}-i(\Phi^B|\,T_BV_B{}^{-1}|\Phi^A)\frac{dA}{dt}\,. \tag{34}$$

We now substitute (18b) for dB/dt in (34) and premultiply by $(\Phi^A|\,V_B|\Phi^B)$, making use of (30) and the closure property of Φ^B, to obtain

$$\begin{aligned}d^2A/dt^2-i(\Phi^A|\,V_BT_BV_B{}^{-1}|\Phi^A)(dA/dt)&\\+(\Phi^A|\,V_BV_A|\Phi^A)A=0\,,&\end{aligned} \tag{35a}$$

which is the desired result. Thus, we have replaced two coupled first-order matrix equations by a single second-order matrix equation. A similar analysis, in which A is eliminated from (18a) and (18b), yields

$$\begin{aligned}d^2B/dt^2-i(\Phi^B|\,V_AT_AV_A{}^{-1}|\Phi_B)(dB/dt)&\\+(\Phi^B|\,V_AV_B|\Phi^B)B=0\,.&\end{aligned} \tag{35b}$$

If we now perform calculations in which only a limited number of elements of Φ^A are retained in the matrices $\langle\Phi^A|\,V_BT_BV_B{}^{-1}|\Phi^A\rangle$ and $(\Phi^A|\,V_BV_A|\Phi^A)$ we already include continuum effects due to the intermediate transitions of (18). Equation (35a) is most useful for calculating excitation amplitudes while (35b) suffers from the difficulty of including the proper boundary conditions and in this respect it resembles (12b). The usefulness of (35a) and (35b) is therefore restricted. To overcome this limitation we must use (24a) and (24b) as our starting equations rather than (18a) and

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[15] Relativistic corrections have been made by M. H. Mittleman, Proc. Phys. Soc. (London) 84, 453 (1964). At extreme relativistic energies the charge-exchange amplitude breaks down and (26) no longer applies. R. A. Mapleton, *ibid.* A264, 272 (1964).

[16] R. Aaron, R. D. Amado, and B. W. Lee, Phys. Rev. 121, 319 (1961).

(18b). In this case the derivation of the second-order equations is somewhat more complicated although the principles involved are similar to those employed above. A simpler derivation, which has the additional advantage of avoiding assumptions about the existence of the inverse matrix, follows from the identities

$$(\Phi^A|V_BT_BV_B^{-1}T_A|\Psi)=(\Phi^A|V_BV_A|\Psi)\,, \quad (36a)$$

$$(\Phi^B|V_AT_AV_A^{-1}T_B|\Psi)=(\Phi^B|V_BV_A|\Psi)\,, \quad (36b)$$

which may easily be verified with the aid of (1a) and (1b). Equations (36a) and (36b) may be considered as the starting point of the second-order theory replacing (10a) and (10b) of the first-order theory. For example, by substituting (6a) in (36a) and (6b) in (36b) we obtain (35a) and (35b), which are the second-order analogs of (12a) and (12b). Similarly, by substituting (23) for Ψ in (36a) and (36b), we obtain the second-order analog of (24a) and (24b). The result is

$$\begin{aligned}(d^2A/dt^2)-i(\Phi^A|V_BT_BV_B^{-1}|\Phi^A)(dA/dt)+(\Phi^A|V_AV_B|\Phi^A)A&\\ =-(\Phi^A|\Phi^B)(d^2B/dt^2)+i(\Phi^A|V_BT_AV_B^{-1}|\Phi^B)(dB/dt)&+(\Phi^A|V_BT_BV_B^{-1}V_A-V_BV_A|\Phi^B)B\,, \quad (37a)\end{aligned}$$

$$\begin{aligned}(d^2B/dt^2)-i(\Phi^B|V_AT_AV_A^{-1}|\Phi^B)(dB/dt)+(\Phi^B|V_AV_B|\Phi^B)B&\\ =-(\Phi^B|\Phi^A)(d^2A/dt^2)+i(\Phi^B|V_AT_BV_A^{-1}|\Phi^A)(dA/dt)&+(\Phi^B|V_AT_AV_A^{-1}V_B-V_BV_A|\Phi^A)A\,. \quad (37b)\end{aligned}$$

Finally, we note the following useful relationships which may easily be verified

$$(\Phi^A|V_BT_AV_B^{-1}|\mathfrak{L})=-i(d(\Phi^A|\ln V_B|\mathfrak{L})/dt)+(\Phi^A|\tfrac{1}{2}V_B^2+(1+\ln V_B)T_A|\mathfrak{L})\,, \quad (38a)$$

$$(\Phi^B|V_AT_BV_A^{-1}|\mathfrak{L})=-i(d(\Phi^B|\ln V_A|\mathfrak{L})/dt)+(\Phi^B|\tfrac{1}{2}V_A^2+(1+\ln V_A)T_B|\mathfrak{L})\,. \quad (38b)$$

V. DETAILED CALCULATIONS

To illustrate the method we calculate $a_{1s}(t)$ by applying the diagonal approximation to (35a). The solution may be regarded as the second-order analog of (13) and is used to calculate inelastic cross sections by substituting it into the appropriate first-order matrix elements. This procedure is slightly inconsistent and the results obtained are not truly representative of the second-order approach. For example, by applying the diagonal approximation to (37a) and (37b), we would have obtained a second-order equivalent of the two-state Bates-McCarroll approximation. However, such a calculation would be rather complex and will therefore be delayed to a later date.

Our equation for $a_{1s}(t)$ is

$$(d^2a_{1s}(t)/dt^2)+(P-iQ)(da_{1s}(t)/dt)+Ha_{1s}(t)=0\,, \quad (39)$$

where

$$\begin{aligned}P&=-(d/dt)(\Phi_{1s}^A|\ln V_B|\Phi_{1s}^A)\,,\\ Q&=(\Phi_{1s}^A|V_B-V_A+\tfrac{1}{2}V_B^2|\Phi_{1s}^A)\,, \quad (40)\\ H&=(\Phi_{1s}^A|V_AV_B|\Phi_{1s}^A)\,.\end{aligned}$$

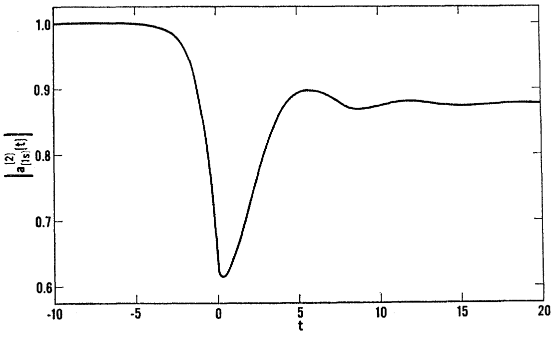

FIG. 1. $|a_{1s}^{(2)}(t)|$ for $v=1$ and $\rho=0.1305$.

It must be solved subject to

$$a_{1s}(t) \underset{t\to-\infty}{\longrightarrow} (vR-v^2t)^{-i/v}. \quad (41)$$

Details are given in the appendix. We denote the result of this second order calculation by $a_{1s}^{(2)}(t)$ to distinguish it from the corresponding first-order result, (13), which we denote by $a_{1s}^{(1)}(t)$.

Figure 1 shows $|a_{1s}^{(2)}(t)|$ for $\rho=0.1305$ and $v=1$. Note the deep trough which occurs just after impact and the slight decaying oscillation which follows as the interproton distance increases and $|a_{1s}^{(2)}(t)|$ settles to a constant, somewhat less than unity. This behavior is typical, the depth of the trough decreasing with increasing impact parameter and velocity. $|a_{1s}^{(1)}(t)|$ is, of course, everywhere unity since, unlike $|a_{1s}^{(2)}(t)|$, it does not share probability with competing inelastic channels.

First- and second-order distortion approximations to the excitation probability $P_A(1s,2s)$, are obtained by replacing $a_{1s}(t)$ of (17) by $a_{1s}^{(1)}$ and $a_{1s}^{(2)}$ and the corresponding cross sections $Q_A^{D_1}(ks,2s)$ and $Q_A^{D_2}(1s,2s)$ are tabulated, together with the first Born cross section,[17] in Table I. $Q_A^{D_1}(1s,2s)$ is smaller than Q_A^B

TABLE I. Cross sections for $H^++H(1s) \rightarrow H^++H(2s)$ in units of πa_0^2.

log [Energy (keV)]	$Q_A^B(1s,2s)$	$Q_A^{D_1}(1s,2s)$	$Q_A^{D_2}(1s,2s)$
1.00	5.37×10^{-1}	6.79×10^{-2}	2.57×10^{-2}
1.25	4.10×10^{-1}	1.31×10^{-1}	5.70×10^{-2}
1.50	2.76×10^{-1}	1.46×10^{-1}	8.08×10^{-2}
1.75	1.72×10^{-1}	1.21×10^{-1}	7.88×10^{-2}
2.00	1.03×10^{-1}	8.42×10^{-2}	6.07×10^{-2}
2.50	3.42×10^{-2}	3.22×10^{-2}	2.58×10^{-2}

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[17] D. R. Bates and G. W. Griffing, Proc. Phys. Soc. (London) **A66**, 961 (1953).

TABLE II. Cross sections for $H^+ + H(1s) \rightarrow H(1s) + H^+$ in units of πa_0^2.

Energy (keV)	5	25	50	100	400	1000
$Q_B^{BK}(1s,1s)$	2.01×10^2	1.68×10^1	3.37	4.00×10^{-1}	1.02×10^{-3}	7.94×10^{-6}
$Q_B^{MBK}(1s,1s)$	5.02	3.81	1.19	1.83×10^{-1}	6.15×10^{-4}	6.87×10^{-6}
$Q_B^{D_1}(1s,1s)$	4.38	4.87	1.52	2.31×10^{-1}	7.86×10^{-4}	8.77×10^{-6}
$Q_B^{D_2}(1s,1s)$	4.02	3.08	1.00	1.55×10^{-1}	5.29×10^{-4}	$5.5\ \times10^{-6}$
$Q_B^{BM}(1s,1s)$	11.3	3.13	7.70×10^{-1}	1.15×10^{-1}	5.38×30^{-4}	5.82×10^{-6}

$\times(1s,2s)$, especially at low energies. This results from the presence of the phase factor in the overlap integral of the former. $Q_A^{D_2}(1s,2s)$ is smaller than $Q_A^{D_1}(1s,2)s$ as a consequence of the allowance for inelastic processes inherent in $a_{1s}^{(2)}(t)$. For comparative purposes, the above results are shown in Fig. 2 together with some calculations of previous authors. It is seen that the distortion approximations are in broad agreement with the $1sA/2sA$ approximation to (12a) and the $1sA/2sA/1sB$ approximation to (24a) and (24b) but show a marked disagreement with treatments which take account of excitation to the $2p$ levels,[8,18] where the computed cross sections are larger than $Q_A^B(1s,2s)$. This is not too surprising, for the optically allowed $1s$-$2p$ transitions are expected to have large cross sections, and since the $2p$ and $2s$ states are degenerate we may expect a strong coupling between these states and a consequent increase in the computed cross section $Q_A(1s,2s)$. However, as we have seen, the second-order treatment has the effect of reducing the cross section in the distortion approximation, and if a similar effect should occur in a second-order calculation with allowance for intermediate $2p$ states it appears likely that the final result may be close to that of the first Born approximation.

For resonant charge transfer we calculate the MBK and distortion cross sections, $Q_B^{MBK}(1s,1s)$ and $Q_B^{D_1}(1s,1s)$, described in Sec. III. The second-order distortion approximation is obtained by substituting $\delta_{n,1s}a_{1s}^{(2)}(t)$ for A in (19). The resultant cross section $Q_B^{D_2}(1s,1s)$ is tabulated together with $Q_B^{MBK}(1s,1s)$, $Q_B^{BK}(1s,1s)$, $Q_B^{D_1}(1s,1s)$, and the Bates-McCarroll cross section $Q_B^{BM}(1s,1s)$ in Table II. Of the above cross sections only $Q_B^{BK}(1s,1s)$ is derived with incorrect boundary conditions for $a_{1s}(t)$ and, as may be seen from the table, it is in considerable disagreement with the other tabulated cross sections over most of the energy region considered. The difference between $Q_B^{D_1}(1s,1s)$ and $Q_B^{D_2}(1s,1s)$ illustrates the distinction between first- and second-order effects. $Q_B^{D_2}(1s,1s)$ is in extremely good agreement with $Q_B^{BM}(1s,1s)$ and this seems to indicate that the back coupling effects of $Q_B^{BM}(1s,1s)$ are largely accounted for in $Q_B^{D_2}(1s,1s)$. However, it should not be concluded from this that these cross sections provide an accurate representation of the exact result since the methods considered have taken no account of contributions from terms other than $a_{1s}(t)$.

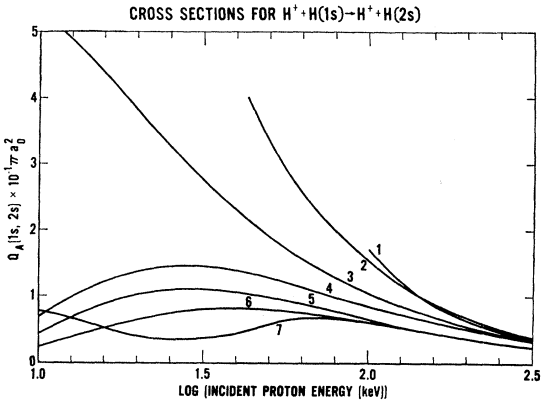

FIG. 2. Cross sections for $H^+ + H(1s) \rightarrow H^+ + H(2s)$. 1—Second Born approximation (Ref. 18); 2—$1sA/2sA/2pA$ approximation (Ref. 8); 3—first Born approximation (Ref. 17); 4—first-order distortion approximation (Ref. 7); 5—$1sA/2sA$ approximation (Ref. 3); 6—second-order distortion approximation; 7—$1sA/1sB/2sA$ approximation (Ref. 3).

Such contributions, if important, should be apparent in a proper two-state calculation based on (37a) and (37b).

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APPENDIX

The coefficients of (40) are found to be

$$P=\frac{\dot{R}}{R}\left(\frac{3}{2}-\frac{3K_1}{4R}-\frac{R}{2}K_0\right)=\frac{d}{dt}\left(\ln R+\frac{1}{4R}(K_0+K_1)\right), \quad \text{(A1)}$$

$$Q=1+e^{-2R}-(1/R)(1-e^{-2R})-(1/2R)K_1, \quad \text{(A2)}$$

$$H=(1/R)(1-e^{-2R}), \quad \text{(A3)}$$

with

$$K_0=e^{2R}E(2R)-e^{-2R}E(-2R), \quad \text{(A4)}$$

$$K_1=\tfrac{1}{2}K_0-R[e^{2R}E(2R)+e^{-2R}E(-2R)], \quad \text{(A5)}$$

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[18] A. E. Kingston, B. L. Moiseiwitsch, and B. G. Skinner, Proc. Roy. Soc. (London) A258, 237 (1960).

and

$$E(x)=\int_x^\infty \frac{1}{y}e^{-y}dy. \tag{A6}$$

Writing

$$a_{1s}=ae^{i\theta}, \tag{A7}$$

we have

$$\ddot{a}+p\dot{a}+(H-\alpha-Q\alpha^2)a=0, \tag{A8}$$

$$\dot{\alpha}+((2/a)\dot{a}+P)\alpha=P(\dot{a}/a), \tag{A9}$$

where

$$\alpha=\dot{\theta}. \tag{A10}$$

The boundary condition (7) implies that as $t\rightarrow-\infty$ $a\rightarrow 1$ and $\alpha\rightarrow 1/R$. With these considerations in mind it was found convenient to introduce

$$y=\alpha a^2R\exp\mathcal{L}, \tag{A11}$$

where

$$\mathcal{L}=(1/4R)(K_0+K_1), \tag{A12}$$

and to replace (A8) and (A9) by three coupled first-order equations

$$\dot{a}=(1/R)\exp(-\mathcal{L})b, \tag{A13}$$

$$\dot{b}=\frac{Qy}{a}+\frac{y^2}{a^3R}\exp(-\mathcal{L})-RaH\exp\mathcal{L}, \tag{A14}$$

$$\dot{y}=-Qab, \tag{A15}$$

and to solve these numerically with the boundary conditions

$$\begin{aligned}&\lim_{t\rightarrow-\infty}a=1,\\&\lim_{t\rightarrow-\infty}y=1,\\&\lim_{t\rightarrow-\infty}b=0.\end{aligned} \tag{A16}$$

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Formula for the Asymmetry in Double Scattering of Fast Electrons by Thomas-Fermi-Dirac Field*

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This note facilitates the calculation of the asymmetry in the double scattering of fast electrons by a Thomas-Fermi-Dirac field.

THE purpose of this note is to give an analytical formula for the asymmetry δ in double scattering[1] of fast electrons by a Thomas-Fermi-Dirac (T.F.D.) field. Using Dirac's equations as well as first and second Born approximation it can be shown that δ is given by[2]

$$\delta=\left(\frac{\alpha Z}{4\pi}\right)^2\frac{\beta^2(1-\beta^2)\sin\vartheta_1\sin\vartheta_2}{(1-\beta^2\sin^2\frac{1}{2}\vartheta_1)(1-\beta^2\sin^2\frac{1}{2}\vartheta_2)}\frac{W(\mathbf{e}_0,\mathbf{e}_1)W(\mathbf{e}_1,\mathbf{e}_2)}{u(\mathbf{e}_0,\mathbf{e}_1)u(\mathbf{e}_1,\mathbf{e}_2)}, \tag{1}$$

where Z is the atomic number, ϑ_1 and ϑ_2 are the scattering angles in double scattering, α is the Sommerfeld fine-structure constant and $\beta=v/c$, ϑ and c are the velocities of electron and light, respectively. The expressions u and W are connected with the first and second Born approximation for the scattering amplitude. The unit vectors $\mathbf{e}_0$, $\mathbf{e}_1$, and $\mathbf{e}_2$ give the direction of the electron momentum before the scattering, after first and second scattering, respectively. Bonham and Strand[3] have shown that the T.F.D. field can be very well approximated by a series of exponential functions

$$V(r)=\frac{Ze^2}{r}f(r)=\frac{Ze^2}{r}\sum_{i=1}^{3}{}^{a}\gamma_i e^{-{}^{a}\lambda_i r}, \tag{2}$$

where e is the electron charge and ${}^{a}\gamma_i$ and ${}^{a}\lambda_i$ are potential parameters depending on Z. The numerical values of

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[1] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, London, 1943).

[2] For reference see: T. Tietz, Acta Phys. Acad. Sci. Hung. **12**, 151 (1960).

[3] R. A. Bonham and T. G. Strand, J. Chem. Phys. **39**, 2200 (1963).