Variational Bounds on the 1*s*—Charge-Exchange Amplitude in Proton-Hydrogen-Atom Scattering*

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With a relatively simple trial wave function, nontrivial variational bounds are obtained on some transition amplitudes for the 1*s*—charge-exchange reaction in the impact-parameter model for H^+-H scattering. Preliminary results imply that the two-state traveling molecular expansion is superior to the two-state traveling atomic expansion below 25 keV, that the Euler-Lagrange variational method is not necessarily superior to the static method, and that neither is the "best variational method."

Proton—hydrogen-atom scattering in the keV energy range is customarily described by the impact-parameter model for ion-atom collisions.[1] Within the framework of the impact-parameter model, it has been possible to derive upper and lower variational bounds which bracket the exact transition amplitudes for the excitation and charge-exchange processes,[2-4] and therefore it is possible, in principle, to calculate exact amplitudes in a variational calculation. In addition, it has been proposed that the error function

$$\Delta_1(\chi_n) = \int_{-\infty}^{\infty} \|D(\chi_n)\| dt \qquad (1)$$

be used as a measure of the error in the calculation in which χ_n is the approximate or trial wave function corresponding to the initial state n.[3-4] The quantity $\|D(\chi_n)\|$ is the norm of the deviation vector in the Schrödinger equation:

$$D(\chi_n) = (H - i\partial/\partial t)(\chi_n - \psi_n) = (H - i\partial/\partial t)\chi_n, \qquad (2)$$

where ψ_n is the exact solution, and H is the Hamiltonian for the impact-parameter—model system.[1] The quantity $\chi_n - \psi_n = \delta\psi_n$ is the variation about the exact solution ψ_n represented by the approximate wave function χ_n; therefore $\|D(\chi_n)\|$ is the error (per unit time) in the Schrödinger equation, and so Δ_1 is a natural measure of the error in the calculation.[3-4] Variational bounds on the exact 1*s*-charge-exchange amplitude A_{1s} can be written as follows[3-4]:

$$|C_{1s}| - \Delta_k \leq |A_{1s}| \leq |C_{1s}| + \Delta_k, \qquad (3)$$

where C_{1s} is a second-order accurate approximation to the exact amplitude A_{1s} obtained with the trial wave function χ_{1s},[3] and Δ_k is either the first-order bound Δ_1 (the error function defined above), or the second-order bound,

$$\Delta_2 = \tfrac{1}{2}\Delta_1^2, \qquad (4)$$

on the second-order error term in the variational principle previously given.[3-4] As previously discussed,[3] trial wave functions are customarily generated by expressing the approximate wave function as a time-dependent linear combination of a suitable finite set of basis functions, and the linear expansion coefficients, which are ultimately interpreted as approximate transition amplitudes, are determined by solving the usual set of coupled equations. In this preliminary study of the 1*s*-charge-exchange reaction, we have been concerned with three questions: (1) What are the magnitudes of the bounds Δ_1 and Δ_2 for some common trial functions, and does it appear to be practical to use the variational bounds in Eq. (3) to calculate exact amplitudes? (2) In what energy range is the traveling-molecular-type expansion superior to the traveling-atomic-type expansion? Aspects of this question have been discussed by Ferguson,[5] McCarroll, Piacentini, and Salin,[6] and McCarroll and Piacentini.[7] (3) Is the Euler-Lagrange dynamic variational method used by Cheshire[8] and by McCarroll, Piacentini, and Salin[6] superior to the static variational method in which the variable parameters in the basis functions are determined by minimizing the well-known energy functional? A simple "two-state" trial wave function was used in all of our calculations. The orbitals in the basis functions were atomiclike functions with variable parameters. The most sophisticated orbital utilized was a 1*s*-hydrogen-like orbital containing a variable nuclear-charge parameter, plus a polarization parameter multiplying a $2p_0$-hydrogen-like orbital containing another variable nuclear-charge parameter.

In our first series of calculations we were only concerned with the effect of a variable nuclear charge in the 1*s* orbital, and so the orbitals were simply 1*s*-hydrogen-like functions with variable nuclear-charge parameters. Some of the values obtained for the error function Δ_1 in these calculations are shown in Fig. 1. The charge-exchange

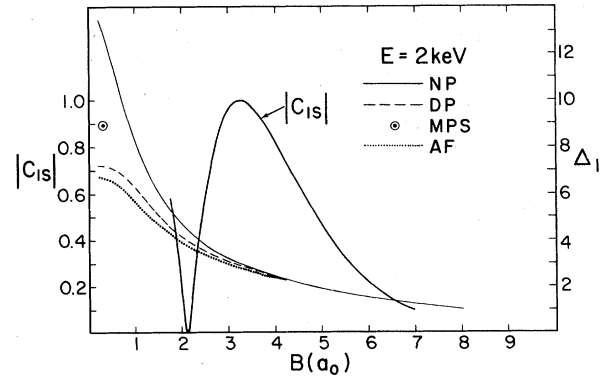

FIG. 1. Absolute value of charge-exchange amplitude $|C_{1s}|$ (corresponding to no-parameter case) and error function Δ_1 for various two-state trial wave functions (see text) versus impact parameter B.

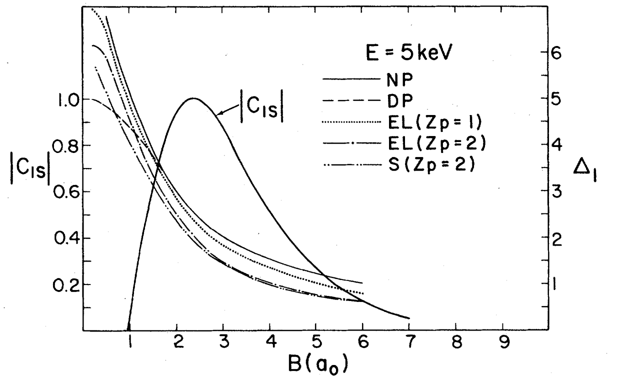

FIG. 2. Absolute value of charge-exchange amplitude $|C_{1s}|$ (corresponding to no-parameter case) and error function Δ_1 for various two-state trial wave functions (see text) versus impact parameter B.

amplitude $|C_{1s}|$ (corresponding to the no-parameter case, see below) is shown in Figs. 1–3 for orientation. The charge-exchange cross section is largely determined by the outer oscillation in the amplitude curve, and so it is these amplitudes that we wish to calculate most accurately. The Δ_1 curve marked NP (no parameters) corresponds to an atomic-type expansion, a two-state traveling hydrogenic expansion. The Δ_1 curve marked DP (Dalgarno and Poots) corresponds to a molecular-type expansion, a two-state traveling molecular expansion where the approximate molecular orbitals are linear combinations of atomiclike functions with nuclear-charge parameters determined by minimizing the energy functional.[9] The point marked MPS corresponds to a calculation in which the variable charge parameters previously given by McCarroll, Piacentini, and Salin[6] were used, and the fact that this point is above the DP curve indicates that within the framework of the two-state approximation the static variational method is superior to the dynamic Euler-Lagrange procedure for this parameter at an energy of 2 keV. The Δ_1 curve marked AF (arbitrary functions) corresponds to a calculation in which arbitrary functions were used for the variable nuclear-charge parameters, and the fact that this curve lies below the DP curve and the MPS point indicates that neither the static nor the dynamic variational methods is best for this problem.

In the second series of calculations we were only concerned with the effect of a polarization parameter; in this case, the orbitals were $1s$-hydrogen-like functions plus a polarization parameter multiplying a $2p_0$-hydrogen-like function. The nuclear scale factors were taken as constants. Some of the results of this calculation are shown in Fig. 2. The Δ_1 curves marked NP and DP again correspond to the same atomic and molecular expansions discussed above. The Δ_1 curve marked S (static) also corresponds to a molecular-type calculation: In this case the approximate molecular orbitals contained only polarization parameters. The Δ_1 curve marked EL (Euler-Lagrange) corresponds to an atomic-type expansion with a dynamically determined polarization parameter. The molecular-type expansions again appear superior to the atomic-type expansions, and the static variational meth-

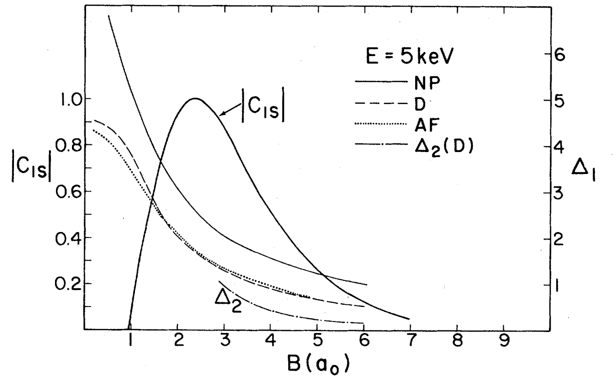

FIG. 3. Absolute value of charge-exchange amplitude $|C_{1s}|$ (corresponding to no-parameter case) and error function Δ_1 for various two-state trial wave functions (see text) versus impact parameter B. Values of the second-order bound Δ_2 are also shown on the same right-hand vertical scale as Δ_1.

od again appears superior to the dynamic Euler-Lagrange procedure.

The most sophisticated orbitals were used in the last series of calculations: The orbitals were 1*s*-hydrogen-like functions with a variable nuclear-charge parameter plus a polarization parameter multiplying $2p_0$-hydrogen-like functions with a variable nuclear-charge parameter. The parameters in the orbitals were determined by minimizing the energy functional,[10] and we believe these orbitals are adequate representations of the $1s\sigma_g$ and $2p\sigma_u$ molecular states. Values of the error function Δ_1 obtained in these calculations are shown in Fig. 3. The Δ_1 curve marked NP again corresponds to the atomic-type expansion discussed above; the Δ_1 curve marked D corresponds to the molecular-type expansion in which the $1s\sigma_g$ and $2p\sigma_u$ orbitals[10] were used; and the Δ_1 curve marked AF again corresponds to a calculation in which an arbitrary set of parameters were used. The fact that the D curve is lower than the NP curve is good evidence that the two-state traveling molecular trial wave function is superior to the two-state traveling atomic trial wave function. We also show values of the second-order bound Δ_2. It is interesting to note that the second-order bound is slightly smaller than the amplitudes in the range of impact parameters 3.5–5. We are extremely encouraged by this result, considering the simplicity of the trial wave function.

In conclusion, our results tend to indicate that the traveling-molecular-type expansion is superior to the traveling-atomic-type expansion in the energy range 0.1–25 keV, and that the dynamic Euler-Lagrange variational method is not necessarily superior to the static method in this energy range. Finally, it is encouraging that a bound Δ_2 which is the same order of magnitude as a transition amplitude can be calculated with such a simple trial wave function. It is well known that the simple two-state approximation is inadequate even for the lower energies.[11-12] With the addition of more states, there is a likelihood that Δ_2 can be reduced to the point where nontrivial bounds on the 1*s*-charge-exchange amplitude can be obtained.

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