Reply to "Limitation on numerical bounds on transition probabilities"

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It is demonstrated that a good share of the error Shakeshaft attributes to the failure to account for ionization in customary impact-parameter calculations for proton-hydrogen-atom scattering amplitudes really results from the inadequacy of the traveling hydrogenic basis set to account for the dynamic polarization of the hydrogen atom by the moving proton. The lower limit for the first-order bound can be reduced by using hydrogenlike basis functions that allow for this polarization. Bounds on the cross sections obtained by using the bound Δ_1 need not be infinite. The inclusion of time-dependent adjustable parameters in the basis functions provides a method for modifying the projection of the deviation vector or error term in the Schrödinger equation in the continuum. The exploratory work of Storm and Rapp appears to offer hope that reasonably accurate bounds on at least the 1s charge exchange amplitudes and cross sections can be obtained by employing only square-integrable basis functions that contain time-dependent variable parameters. However, if it is necessary to account for the flux in the ionization channels, it is shown that an account could be made without the bound becoming infinite.

It has been possible to derive upper and lower variational bounds which bracket the exact transition amplitudes[1] in a time-dependent quantum-mechanical problem,[2-4] and the magnitude of these bounds on the 1s charge exchange amplitudes in the semiclassical impact-parameter model for proton-hydrogen-atom scattering have been calculated by Storm and Rapp.[5] The fact that it was possible to obtain bounds on the error term that were comparable to the magnitudes of the approximate amplitudes using simple trial wave functions[6] seemed to us to offer hope that the indirect variational approach might prove fruitful in this problem.

In the preceding comment,[7] Shakeshaft states that he examines the effect of the neglect of ionization in the customary calculation, and he finds it to be significant. Since it does not appear to him to be possible to take ionization into account without the bounds becoming infinite, he concludes that the numerical bounds must necessarily be of limited accuracy.

Our own research, however, indicates that the assumptions upon which Shakeshaft's analysis rests are unnecessarily restrictive, and can be easily modified to reduce the effect he calculates. It will be shown that most of the effect Shakeshaft attributes to ionization is really related to the polarization of the hydrogen atom by the moving proton. The question of the need to account for ionization and how an approximate account could be made will also be briefly discussed. At this stage in the development of an indirect variational approach for this model problem, it appears to us to be premature to conclude that the numerical bounds must necessarily be of limited accuracy.

We will now consider Shakeshaft's argument in greater detail. The bound B in Eq. (6) of Ref. 7 is also the previously discussed error function[3,4]:

$$\Delta_1(X_i) = \int_{-\infty}^{\infty} \|D(X_i)\| dt \,, \tag{1}$$

where $D(X_i)$ is the deviation vector or error term in the Schrödinger equation when the trial wave function X_i is substituted into the equation. The magnitude of Δ_1 is a measure of how well the trial solution approximates the exact wave function uniformly; the magnitudes of the errors in the approximate amplitudes are bounded by Δ_1. To investigate the effect of ionization Shakeshaft inserts the complete set of eigenfunctions of the target hydrogen-atom Hamiltonian $\{\phi_n\}$:

$$\|D(X_i)\| = \left(\sum_n |\langle \phi_n | D(X_i)\rangle|^2\right)^{1/2} . \tag{2}$$

It is important to note at this point that the mathematical projections of the deviation vector in the continuum of the basis in which we choose to represent the deviation vector are not necessarily related to the physical ionization process. Now, the trial wave functions employed by Storm and Rapp[5] were linear combinations of orbitals with the following form:

$$\chi_{1s} = [\phi_{1s}(Z_s) + \sigma\phi_{2p_0}(Z_p)]\, e^{-i\epsilon_{1s}t} \,,$$
$$\epsilon_{1s} = -\tfrac{1}{2}Z_s^2 \,, \tag{3}$$

where ϕ_{1s} and ϕ_{2p_0} are 1s and 2p_0 hydrogenlike functions, and the scale factors Z_s and Z_p and the

polarization parameter σ are time-dependent variable parameters. The basis orbital X_{1s} can be viewed as a variable pseudostate that approaches the hydrogenic state ϕ_{1s} as $t \to \infty$. It should be noted that the above basis orbital has projections into the hydrogenic continuum; although it does not represent an ionized state of the hydrogen atom.

By straightforward but extensive analysis, the details of which we intend to report later, we find that the norm of the deviation vector has the following asymptotic forms:

$$\|D\| \sim \beta/R^2 + O(1/R^3), \quad \text{as } |t| \to \infty, \tag{4}$$

where

$$\beta = \begin{cases} 1; & \sigma = 0 \\ \{1 + (A^2/\Omega_{31}^2)[\tfrac{1}{12}Z_p^2(Z_p-1)^2 + \omega_{31}^2 + \tfrac{1}{2}Z_p(Z_p-1)\omega_{31}] - \tfrac{1}{4}(A^2/\Omega_{31})(2+Z_p)(Z_p-1) - 2(A^2/\Omega_{31})\omega_{31}\}^{1/2}; \\ \qquad \sigma \sim (A/\Omega_{31})1/R^2 \quad \text{as } |t| \to \infty, \end{cases} \tag{5}$$

with

$$A = 128\sqrt{2}\, Z_p^{5/2}/(2+Z_p)^5,$$
$$\Omega_{31} = \tfrac{1}{4}Z_p(Z_p-1) + \omega_{31}, \tag{6}$$
$$\omega_{31} = \epsilon_{2p} - \epsilon_{1s}.$$

For $Z_p = 1.56$, we find that $\beta = 0.15$; this result should be contrasted to the statement in Ref. 7 that if ionization is neglected, the minimum value of this constant is 0.53. It is clear that while we have not allowed for ionization with this type of trial wave function, we have allowed for a crude account of the physical effect of the dynamic polarization of the hydrogen atom by the moving proton. Furthermore, by referring to Shakeshaft's analysis in his Eqs. (8)–(20), it is clear that our Eq. (4) indicates that we have been able to modify the projection of the deviation vector into this continuum by employing only square-integrable basis functions. Shakeshaft's conclusion concerning the importance of ionization follows from the unnecessarily restrictive assumption in Eqs. (10) and (11) that the state of the system is described by the ground-state wave function of the hydrogen atom.

Although it may not be immediately apparent from Eqs. (2)–(6), the quantity β in Eqs. (4)–(6) is influenced by the choice of the phase factors in the basis orbitals. The over-all phase factor in the trial wave function is lost when the norm of the deviation vector is formed; however, the relative phase information in the basis functions is not lost, since the operator $(H - i\,\partial/\partial t)$ acts upon the basis functions. For example, suppose one allows the polarization parameter to be complex:

$$\chi_{1s} = [\phi_{1s}(Z_s) + \sigma e^{ift}\phi_{2p_0}(Z_p)]\, e^{-i\epsilon_{1s}t}. \tag{7}$$

In this case we find that

$$\|D\| \sim \beta'(t)/R^2 + O(1/R^3), \quad \text{as } |t| \to \infty, \tag{8}$$

where

$$\beta'(t) = \{1 + (A^2\cos^2 ft/\Omega_{31}'^2)[\tfrac{1}{12}Z_p^2(Z_p-1)^2 + \omega_{31}^2 + \tfrac{1}{2}Z_p(Z_p-1)\omega_{31} + (f + t\,df/dt)^2]$$
$$- \tfrac{1}{4}(A^2\cos^2 ft/\Omega_{31}')(2+Z_p)(Z_p-1) - 2(A^2\cos^2 ft/\Omega_{31}')\omega_{31}\}^{1/2}; \quad \sigma \sim (A/\Omega_{31}')\cos ft/R^2 \tag{9}$$

$$\Omega_{31}' = \tfrac{1}{4}Z_p(Z_p-1) + \omega_{31} - f - t\,df/dt. \tag{10}$$

It should be clear from this analysis and the result of Ref. 7 obtained with molecular basis functions, Eq. (22), that the slow decrease of Δ_1 with impact parameter results from the choice of hydrogenic basis functions. Thus the bounds on the cross sections need not necessarily be infinite. One might hope, at least in initial work, that the flux in the ionization channels is small,[8] and therefore the magnitude of the error in the asymptotic region is small. Thus, with the increased flexibility offered by the use of adjustable parameters in the basis functions, it might be possible to adequately account for continuum effects, and thereby obtain reasonably accurate bounds on at least the 1s charge exchange amplitudes and cross sections. This avenue of research has not been fully explored; the flexibility to tailor a trial wave function by including time-dependent adjustable parameters in the basis functions has only been crudely exploited in initial work.[5]

However, if the flux in the ionization channels is too large, or if one cannot account for continuum effects by this indirect approach, then one must include in some manner continuum basis functions in the trial wave function. Now by starting with the Lippman-Schwinger equation for the three-particle proton–hydrogen atom system in forms in which the amplitudes for excitation and charge exchange are explicitly displayed, it was previously shown how the corresponding impact-parameter amplitudes for excitation and charge exchange are displayed in the impact-parameter

wave function.[9] As previously discussed, approximate amplitudes are obtained from a trial wave function X_i which is selected from the class of functions $[X]$ that have the same asymptotic forms as the impact-parameter wave function.[3] Since it is easy to choose trial wave functions that satisfy these boundary conditions, one has no difficulty in ensuring that the deviation vector vanishes as $|t|\to\infty$, and the error function $\Delta_1(X_i)$ is finite. However the work of Temkin,[10] who studied the asymptotic form of the time-independent wave function for the electron-ionized hydrogen atom system, indicates that it will be difficult to find in an analogous manner the asymptotic form of the impact-parameter wave function in which the impact-parameter ionization amplitudes are explicitly displayed. Thus, as argued in Ref. 7, it would therefore be difficult to select a suitable trial wave function in which approximate ionization amplitudes are explicitly displayed, since one does not know the boundary conditions that the trial wave function must satisfy; and it is likely that the deviation vector would not vanish as $|t|\to\infty$, and hence the error function might be infinite.

However, it should be noted that the impact-parameter model and wave function are well defined.[9] Furthermore, just as in the case of excitation or charge exchange, the error function $\Delta_1(X_i)$ is defined upon the class of possible trial wave functions $[X]$ [3,4]; thus, for the particular trial wave function X_i to be acceptable, the error function $\Delta_1(X_i)$ must be finite and our problem is to find such functions. We assume that in the asymptotic region ionization should be described by a wave packet; let this basis function be

$$\chi_{\vec{p}_0}(\vec{r},t)=\left(\frac{1}{2\pi}\right)^{3/2}\int d^3p\,\chi(\vec{p})\phi_{\vec{p}}(\vec{r})e^{-i\epsilon t}\,, \tag{11}$$

where $\chi(\vec{p})$ is a distribution function selected such that the wave packet is essentially localized in a small region about the point

$$\vec{r}_0=\tfrac{1}{2}p_0^2\,t\hat{p}_0\,, \tag{12}$$

where $\vec{r}_0$ and $\vec{p}_0$ are the average position and momentum of the wave packet. Suitable eigenfunctions $\phi_{\vec{p}}$ have already been given by Salin.[11] The most offensive part of the norm of the deviation vector in the asymptotic region is therefore

$$\left\langle\left(\frac{Z(\hat{r},\hat{v},\alpha)}{r}-\frac{1}{|\vec{r}+\vec{R}(t)|}\right)\chi_{\vec{p}_0}\right. \times\left.\left|\left(\frac{Z(\hat{r},\hat{v},\alpha)}{r}-\frac{1}{|\vec{r}+\vec{R}(t)|}\right)\chi_{\vec{p}_0}\right\rangle^{1/2}\right. \tag{13}$$

and for a sufficiently narrow wave packet this is approximately given by

$$\cong[Z(\hat{r}_0,\hat{v},\alpha_0)/r_0-1/|\vec{r}_0+\vec{R}(t)|]\,. \tag{14}$$

As described by Salin,[11] the function Z should be

$$Z(\hat{r}_0,\hat{v},\alpha_0)=(|\hat{r}_0-\hat{v}/\alpha_0|)^{-1}\,, \tag{15}$$

where

$$\alpha_0=\lim_{\substack{t\to\infty\\ |\vec{r}_0+\vec{R}(t)|\to\infty}}\frac{r_0}{R}\,. \tag{16}$$

By using Eq. (12) it can be shown that this term in the norm of the deviation vector decreases faster than $1/t$ as $t\to\infty$; hence the error function Δ_1 will be finite. We conclude therefore that it is possible at least conceptually to account for ionization in the impact-parameter model.

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[1]In actuality, the bounds are upon the moduli of the exact amplitudes; however, this distinction is customarily not stated.

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