Limitation on numerical bounds on transition probabilities*

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The effect of neglecting ionization in the calculation of numerical bounds on transition probabilities is examined for proton–hydrogen-atom scattering, and it is found to be significant. This implies that numerical bounds on transition probabilities must necessarily be of limited accuracy, since it does not appear to be possible to take ionization even partially into account without the bounds becoming infinite.

Ion-atom scattering is often described within the impact-parameter approximation of treating the nuclei as classical particles which move with constant velocity. Within this approximation rigorous upper and lower bounds on the transition probabilities of a system have been derived.[1] These bounds were first used to investigate formally the energy dependence of cross sections at high energies,[2] but the question has naturally arisen as to whether one can calculate accurate *numerical* bounds on the transition probabilities of simple systems.

Recently, Storm and Rapp[3] have calculated numerical bounds on the probability for ground-state–ground-state charge transfer in proton–hydrogen-atom scattering. At each energy and impact parameter considered, the bounds on the absolute value of the transition amplitude differ by at least 100% from the corresponding trial estimates. The purpose of this comment is to show by estimating the importance of the ionization channels, that a nontrivial part of the error in the bounds must be due to the neglect of ionization. This implies that numerical bounds on transition probabilities must necessarily be of limited accuracy since it does not appear to be possible to take ionization even partially into account without the bounds becoming infinite.[4]

Ionization must occur within the impact-parameter approximation since within this approximation the Hamiltonian is time dependent so that the energy of the system is not conserved and all channels are open. The probability of ionization may, of course, be small and may not appreciably influence the probability of a transition to a low-lying bound state. However, although the trial estimate of a transition probability may still be quite accurate when ionization is neglected, the corresponding bounds may possibly be inaccurate. In fact, as will be seen below, the manner by which the bounds are obtained removes an over-all multiplicative phase factor from the trial wave function and thereby magnifies the error of neglecting continuum contributions. To see this in more detail we investigate the proton–hydrogen-atom system. We must

first introduce some notation.

We work in the coordinate frame in which the target proton is at rest. The incident proton moves with a constant velocity $\vec{v}$ and an impact parameter $\vec{b}$ relative to the target proton. Let $\vec{r}$ and $\vec{R}(t)$, respectively, be the position vectors of the electron and the incident proton relative to the target proton. We have $\vec{R}(t) = \vec{b} + \vec{v}t$, where t is the time, and the Hamiltonian is defined in atomic units by

$$H(t) \equiv -\tfrac{1}{2}\nabla_{\vec{r}}^2 - \frac{1}{r} - \frac{1}{|\vec{r} - \vec{R}(t)|} + \frac{1}{R(t)} . \tag{1}$$

Let $|\Psi_{\mathrm{tr}}(t)\rangle$ denote the trial state vector of the electron. We assume that $|\Psi_{\mathrm{tr}}(t)\rangle$ is a linear combination of N specified normalizable basis vectors $|\phi_n(t)\rangle$, $n = 1, \ldots, N$, with time-dependent coefficients $a_n(t)$, $n = 1, \ldots, N$ that are determined from the standard coupled-state equations. We have

$$|\Psi_{\mathrm{tr}}(t)\rangle = \sum_{n=1}^{N} a_n(t) |\phi_n(t)\rangle , \tag{2}$$

and the standard coupled-state equations can be written in compact form as

$$P(t)h(t)|\Psi_{\mathrm{tr}}(t)\rangle = 0 , \tag{3}$$

where

$$h(t) \equiv H(t) - i\frac{\partial}{\partial t} ,$$

and where $P(t)$ is the projection operator which projects onto the space spanned by the basis vectors. Since we neglect ionization, the basis vectors represent bound states of the electron in the separated atom limits. Let the initial state i of the electron be represented by the state vector $|\Phi_i(t)\rangle$. Then Eq. (3) is solved subject to the boundary condition

$$|\Psi_{\mathrm{tr}}(t)\rangle \to |\phi_i(t)\rangle \to |\Phi_i(t)\rangle \quad \text{as } t \to -\infty. \tag{4}$$

Let A denote the exact amplitude for the electron to transfer to some (bound) state f represented by the state vector $|\Phi_f(t)\rangle$. The trial approximation to A, obtained by solving the coupled state equations, is

$$A_v = \lim_{t \to \infty} \langle \Phi_f(t) | \Psi_{tr}(t) \rangle , \qquad (5)$$

where the subscript v emphasizes the well-known[5,6] fact that A_v is a variational estimate of A. Spruch[1] has derived the following upper and lower bounds on A:

$$|A_v| - B \le |A| \le |A_v| + B , \qquad (6)$$

where B is a bound on the error in $|A_v|$ and is defined by

$$B \equiv \int_{-\infty}^{\infty} dt \, \| h(t) | \Psi_{tr}(t) \rangle \| , \qquad (7)$$

where $\| \, |\chi\rangle \, \| = \langle \chi | \chi \rangle^{1/2}$ for arbitrary $|\chi\rangle$. Note that we have suppressed the dependence of A, A_v, and B on b and v. Note also that the error in A_v is of second order in the error in Ψ_{tr}, whereas B is only of first order in the error in Ψ_{tr}. An improved (second-order) bound on the error in A_v has also been obtained.[1] However, although there are notable exceptions,[1,6] in general, the improved bound is considerably more difficult to compute than B, and for most of this paper we confine our attention to the simple bound B.

Let $Q(t)$ be the projection operator which projects onto the complement of the space spanned by the basis vectors. Then $P(t) + Q(t) = 1$, and from Eqs. (3) and (7) we have

$$B = \int_{-\infty}^{\infty} dt \, \| Q(t) h(t) | \Psi_{tr}(t) \rangle \| . \qquad (8)$$

Now since $Q(t) | \phi_n(t) \rangle = 0$, we have

$$Q(t) h(t) | \Psi_{tr}(t) \rangle = \sum_{n=1}^{N} a_n(t) Q(t) h(t) | \phi_n(t) \rangle . \qquad (9)$$

Assume first that the basis vectors represent atomic states. Then if $\phi_n(t)$ is centered about the target proton and if $R(t)$ is large, we have

$$h(t) | \phi_n(t) \rangle = \left(\frac{1}{R(t)} - \frac{1}{|\vec{r} - \vec{R}(t)|} \right) | \phi_n(t) \rangle$$

$$= \left[-\frac{\vec{r} \cdot \hat{R}(t)}{R(t)^2} + O\left(\frac{r^2}{R^3} \right) \right] | \phi_n(t) \rangle . \qquad (10)$$

Equation (10) is not valid if the basis vectors represent molecular states; this case will be briefly discussed below. In the limit of either large b or large negative vt we have (if, as assumed throughout, the initial state i is the ground state)

$$a_n(t) = \delta_{ni} + O(1/R^2) .$$

However, if $\phi_n(t)$ is centered about the incident proton, $a_n(t)$ decreases *exponentially* as b or

$-vt \to \infty$, and it follows from Eqs. (9) and (10) that in either of these limits we have

$$\| Q(t) h(t) | \Psi_{tr}(t) \rangle \| = c/R(t)^2 + O(1/R^3) , \qquad (11)$$

where

$$c = \lim_{R \to \infty} \| Q(t) [\vec{r} \cdot \hat{R}(t)] | \Phi_i(t) \rangle \| . \qquad (12)$$

The coefficient c is independent of t since in the limit $t \to -\infty$ or $b \to \infty$ the expression $Q(t) [\vec{r} \cdot \hat{R}(t)] | \Phi_i(t) \rangle$ depends on t only through the phase factor of the initial-state vector. This phase factor has the form e^{-iat}, where a is the initial binding energy of the electron.

To obtain a rough lower estimate of B we neglect the term $O(1/R^3)$ in Eq. (11) if b or $-vt$ is greater than some value R_0. It then follows from Eqs. (8) and (11) that

$$B > \int_{-\infty}^{-R_0/v} dt \, \| Q(t) h(t) | \Psi_{tr}(t) \rangle \|$$

$$\approx \int_{-\infty}^{-R_0/v} \frac{c}{R(t)^2} dt . \qquad (13)$$

If $b \ll R_0$, we obtain from Eq. (13)

$$B \gtrsim c/v R_0 . \qquad (14)$$

On the other hand, if $b > R_0$, we have, using Eqs. (8) and (11),

$$B \approx \int_{-\infty}^{\infty} \frac{c}{R(t)^2} dt = \frac{\pi c}{vb} . \qquad (15)$$

Note that A decreases exponentially with increasing b, whereas according to Eqs. (6) and (15) the bounds on A decrease as $1/b$. Hence these bounds become exceedingly poor with increasing impact parameter and since $\int_0^{\infty} B^2 b \, db = \infty$ they do not give finite bounds on the cross section. The slow decrease with impact parameter is a consequence of the fact that the over-all phase factor of the trial wave function is not present in the expression on the right-hand side of Eq. (11). If a is real and positive, we have

$$\int_{-\infty}^{\infty} dt \frac{e^{iat}}{R(t)^2} = \frac{\pi e^{-ab/v}}{vb} \qquad (16)$$

and it is the absence of the phase factor e^{iat} in the integrand of Eq. (15) which magnifies the contribution from neglected channels and leads to the slow decrease with b.

We now calculate the minimum value of c, that is, we calculate the value of c when, in the asymptotic limits, the basis vectors span the entire space of bound states. Then in the limit $t \to -\infty$, $Q(t)$ projects onto the space spanned by just the continuum states of the hydrogen atom, and if the initial state is the ground state Eq. (12) becomes

$$c_{\min}^2 = \int d\vec{k} \, |f(\vec{k})|^2 \, , \tag{17}$$

where $c_{\min}$ denotes the minimum value of c and where

$$f(\vec{k}) = 2^{-3/2} \pi^{-2} e^{\pi/2k} \Gamma(1 + i/k)$$

$$\times \int d\vec{r}(\vec{r} \cdot \hat{R}) e^{-r + i\vec{k} \cdot \vec{r}} {}_1F_1(-i/k, 1, -i(kr + \vec{k} \cdot \vec{r})). \tag{18}$$

The integral of Eq. (18) can be evaluated by standard methods[7] to yield

$$f(\vec{k}) = i2^{5/2} (\hat{k} \cdot \hat{R}) e^{\pi/2k} \frac{(k+i)\Gamma(1+i/k)}{\pi(k^2+1)^3} \left(\frac{i-k}{k+i}\right)^{i/k} . \tag{19}$$

Substituting the right-hand side of Eq. (19) into Eq. (17) and performing the integration over the angular coodinates, we obtain

$$c_{\min}^2 = \frac{2^8}{3} \int_0^\infty \frac{k \, dk \, e^{-(4/k)\tan^{-1}k}}{(1 - e^{-2\pi/k})(k^2+1)^5} \, . \tag{20}$$

The integral of Eq. (20) can be evaluated numerically to yield $c_{\min} = 0.53$. For a lab energy of 1 keV we have $v \approx 0.2$ a.u. and for this energy it seems reasonable to take R_0 to be 25 a.u. Using these values in Eq. (14) we obtain the conservative estimate $B \gtrsim 0.11$ for small impact parameters and an energy of 1 keV. For large impact parameters we have, inserting the above values in Eq. (15), $B \approx 8.3/b$. Now a convenient measure of the quality of the bounds on $|A|$ is provided by the quantity $|B/A_v|$. Since the maximum value of $|A_v|$ is unity it is clear from the above that if the continuum channels are neglected at large internuclear separations, the bounds will not be very accurate.

Note that B decreases as $1/v$ with increasing v. However, $|A|$ decreases as $(\ln v)/v$, $1/v$, or $1/v^{11/2}$ depending on whether the transition is optically allowed excitation, optically forbidden excitation, or charge transfer. It is therefore unlikely that the bounds improve much as v increases. However, at low energies the bounds can be improved somewhat by using molecular basis vectors. It the basis vectors are formed from *exact* eigenstates of $H(t)$, Eq. (10) should be replaced by

$$h(t) \, | \, \phi_n(t) \rangle = - [i\vec{v} \cdot \nabla_{\vec{R}} + O(1/R^4)] | \phi_n(t) \rangle \, . \tag{21}$$

For large b or negative vt we then obtain

$$\| Q(t)h(t) \, |\Psi_{tr}(t)\rangle \| = \frac{c'v}{R(t)^3} \left[1 + 6\left(\frac{vt}{R(t)}\right)^2 \right]^{1/2} + O\left(\frac{1}{R^4}\right) , \tag{22}$$

where c' is independent of v, t, and b. Thus the coefficient c of the $1/R^2$ term appearing in Eq. (11) vanishes, a consequence of having partially accounted for the continuum at large but finite internuclear separations. It follows that in this case $B \approx 3.3c'/b^2$ for large b. We find that $c' = (\frac{21}{4})^{1/2}$ if only the lowest σ_u and σ_g states are included in the coupled-state expansion.

As we mentioned earlier, it does not appear to be possible to take ionization into account. This is because the integral of Eq. (4) is finite if, and only if,

$$\lim_{t \to \pm\infty} t \, \| h(t) \, | \Psi_{tr}(t)\rangle \| = 0 \, . \tag{23}$$

Equation (23) implies that in both the limits $t \to \infty$ and $t \to -\infty$ the trial state vector $|\Psi_{tr}(t)\rangle$ must *exactly* satisfy a possible boundary condition of the electron. However, the boundary condition appropriate to ionization is extremely complicated,[8] if indeed it is known.[9] Hence it does not appear to be possible to take ionization into account without the bound B becoming infinite.

Up to now, we have only discussed a first-order bound on the error in A_v. As mentioned above, a second-order bound, which we denote by $B^{(2)}$, has also been derived.[1] Roughly speaking, $B^{(2)} \approx B^2$. It is not difficult to show by an analysis similar to the above that $B^{(2)}$ behaves with increasing v and b as $1/(vb)^2$ unless exact molecular basis vectors are used, in which case $B^{(2)}$ behaves as $1/b^4$. Note that for direct transitions, that is, excitation, the quantity $B^{(2)}/A_v$ tends to zero as $v \to \infty$ (unless molecular basis vectors are used). Therefore, when excitation is considered, second-order bounds become extremely accurate as v increases. Furthermore, $B^{(2)}$ decreases sufficiently fast with impact parameter to enable one to obtain a finite bound on the cross section, which is what one really wants. However, although $B^{(2)}$ represents a considerable improvement over B, it still decreases slowly with increasing b, and in general $B^{(2)}$ is much more difficult to compute than B. (Note, however, for very large b the error in A_v is small and, with the sacrifice of rigor, one can neglect the error in A_v.)

In conclusion, because of the manner by which the bounds are obtained, it appears to be very difficult to obtain accurate rigorous numerical bounds on transition probabilities and hence cross sections. We have shown that the ionization channels strongly influence the magnitude of the bounds and their behavior at large impact parameters. This in turn implies that the neglect of ionization will strongly influence the magnitude and behavior of the bounds, and since it does not appear to be possible to account for ionization it follows that the

bounds must be of limited accuracy. The contribution to the second-order bound $B^{(2)}$ arising from the neglect of ionization will obviously be much less than the contribution to the first-order bound B but, whatever its magnitude is, it cannot be reduced indefinitely and, as we have stressed above, in general $B^{(2)}$ is much more difficult to calculate than B.

Note added in proof. In Eqs. (11) and (15) above, the coefficient c is greater than 0.53 if, as is the case when the basis functions represent bound states of the atom, the projection of the trial wave function onto the continuum tends to zero more rapidly than $1/R^2$ as the internuclear separation R increases. In his reply, Storm has shown that c can be reduced below 0.53 by choosing a trial wave function whose projection onto the continuum tends to zero as $1/R^2$ with increasing R. However, this is already evident from the work above, where it has been shown that c vanishes if basis functions which are exact eigenstates of $H(t)$ are used! It should be emphasized that even in this case the contribution from the excluded continuum channels is non-negligible at large R, and the bound B decreases slowly, i.e., as $3.3c'/b^2$, with increasing b. It follows that the accuracy of the bounds is limited by the need to account for the projection of the true wave function onto the continuum as $R \rightarrow \infty$, and hence by the need to account for ionization. Of course, in principle this limitation can be overcome by constructing a wave packet which has the boundary conditions appropriate to ionization. However, it is doubtful that this could be achieved in practice and it is certainly not clear how to proceed from Storm's discussion. In fact, Storm's discussion of this point is based on the untenable assumption that one can construct a wave packet that is not only localized in both momentum and coordinate space, but that remains so localized for an infinite time.

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