# Variational bounds on transition amplitudes*

David Storm
*The University of Texas at Dallas, P. O. Box 688, Richardson, Texas 75080*
(Received 25 March 1974)

Upper and lower variational bounds on the transition amplitudes of the impact-parameter model for ion-atom scattering were recently reported. A comparison of these bounds with those given by Spruch leads to an improved first-order variational bound on the second-order error term in the variational principle recently given. In addition, the second-order variational bound obtained by Spruch from an apparently different second-order error term also follows from this second-order error term. Finally, as Spruch has suggested, the second-order bound is simply given as one-half the first-order bound squared for those amplitudes corresponding to a rearrangement from state $n$ of one arrangement channel to state $n$ of another arrangement channel.

Upper and lower variational bounds which bracket the exact transition amplitudes of the impact-parameter model for ion-atom scattering were given in a recent publication.[1] Unfortunately, when these results were reported, I was not aware that other variational bounds had been previously given. In fact, Aspinall and Percival[2] have given an upper variational bound on the total probability for transitions out of the initial state, and Spruch[3] has derived both upper and lower, nonstationary and stationary variational bounds on the transition amplitudes in a general time-dependent problem.

A comparison of the bounds in Ref. 1 with those given by Spruch[3] is not only interesting in itself, but for the impact-parameter model leads to an improved first-order bound on the second-order error term in the variational principle of Ref. 1. This variational principle can be written as follows:

$$A_{mn} = C_{mn} - iR(\chi_{mR}, \chi_n) + i\Delta(\delta\psi_{mR}, \delta\psi_n)\,, \tag{1}$$

where $A_{mn}$ is the exact amplitude for the $n$-to-$m$ transition, $C_{mn}$ is a first-order approximation to $A_{mn}$, and $R(\chi_{mR}, \chi_n)$ is a correction to the first-order approximation $C_{mn}$, which is given by

$$R(\chi_{mR}, \chi_n) = \frac{1}{\hbar}\int_{-\infty}^{\infty} \langle \chi_{mR} | H - i\hbar \frac{\partial}{\partial t} | \chi_n \rangle\, dt\,; \tag{2}$$

$\chi_{mR}$ and $\chi_n$ are trial wave functions ($\chi_{mR}$ is a time-reversed trial wave function), and $H$ is the Hamiltonian for the impact-parameter model.[1] The quantity $\Delta$ in Eq. (1) is a second-order error term:

$$\Delta = \frac{1}{\hbar}\int_{-\infty}^{\infty} \langle \delta\psi_{mR} | H - i\hbar \frac{\partial}{\partial t} | \delta\psi_n \rangle\, dt\,, \tag{3}$$

where $\delta\psi_{mR}$ and $\delta\psi_n$ are the variations about $\psi_{mR}$ and $\psi_n$ represented by the trial wave functions $\chi_{mR}$ and $\chi_n$.[1] Equation (1) was derived under one restriction: It was assumed that the system is invariant to a reversal of time. A real basis set was employed in the derivation only for convenience. If other phase conventions are used for the time-reversed basis vectors,[4,5] then only the phases of the quantities in Eq. (1) would be changed. Upper and lower bounds follow from Eq. (1):

$$|C_{mn} - iR| - \Delta' \leq |A_{mn}| \leq |C_{mn} - iR| + \Delta'\,, \tag{4}$$

where $\Delta'$ is *some* bound on the second-order error term $\Delta$. The following first-order variational bound on $\Delta$ was given in Ref. 1:

$$\Delta_M = \frac{2}{\hbar}\int_{-\infty}^{\infty} \|D\|\, dt\,, \tag{5}$$

where $\|D\|$ is the norm of the deviation vector in the time-dependent Schrödinger equation:

$$D = \left(H - i\hbar\frac{\partial}{\partial t}\right)(\chi_n - \psi_n) = \left(H - i\hbar\frac{\partial}{\partial t}\right)\chi_n\,. \tag{6}$$

Spruch has given the following variational bounds on the amplitudes[3]:

$$|C_{mn}| - \Delta_1 \leq |A_{mn}| \leq |C_{mn}| + \Delta_1\,, \tag{7}$$

where $\Delta_1$ is a first-order variational bound on a *first-order error term*, and is given by

$$\Delta_1 = \frac{1}{2}\Delta_M = \frac{1}{\hbar}\int_{-\infty}^{\infty} \|D\|\, dt\,. \tag{8}$$

(For convenience I have taken the liberty of modifying Spruch's notation.) As previously discussed, one can determine trial wave functions in a manner that ensures that $R = 0$.[1] Therefore by comparing Eqs. (4), (5), and (7), it is seen that $\Delta_1$ provides an improved bound on the second-order error term $\Delta$; i.e., in the special case where $R = 0$, $\Delta_1$ is a first-order variational bound on the second-order error term $\Delta$. In addition, as previously discussed, the norm of the deviation vector $D$ is a measure of the error (per unit time) in the Schrödinger equation.[1] Therefore, $\Delta_1$ is a natural measure of the error in a calculation in which $\chi_n$ is the trial wave function.

Spruch has also derived a second-order variational bound on a second-order error term in a variational principle which appears to be different from Eq. (1).[3] It is interesting to note that this second-order bound also follows from the second-order error term in Eq. (1). For from Eq. (3):

$$|\Delta'| \leq \frac{1}{\hbar} \int_{-\infty}^{\infty} \|\delta\psi_{mR}\| \, \|D(\chi_n)\| \, dt$$

and

$$\|\delta\psi_{mR}\| = -\int_t^{\infty} \frac{d}{dt'} \|\delta\psi_{mR}(t')\| \, dt' ,$$

where

$$-\frac{d}{dt}\|\delta\psi_{mR}(t)| = \frac{1}{\hbar}\,\frac{\operatorname{Im}\{\langle\delta\psi_{mR}|D(\chi_{mR})\rangle\}}{\|\delta\psi_{mR}\|} \leq \frac{1}{\hbar}\|D(\chi_{mR})\| ;$$

hence

$$|\Delta'| \leq \Delta_2 = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \, \|D(\chi_n)\| \int_t^{\infty} dt' \|D(\chi_{mR})\| , \quad (9)$$

which, under the restriction imposed by time-reversal invariance, is the second-order variational bound given by Spruch.[3] Stationary variational bounds on the transition amplitudes follow by using $\Delta_2$ in Eq. (4).

In general, it will be much more difficult to calculate the second-order bound $\Delta_2$ than the first-order bound $\Delta_1$; one will have to solve two sets of coupled equations to determine the two trial wave functions $\chi_{mR}$ and $\chi_n$, and then perform the double time integration indicated in Eq. (9). However, for certain transition amplitudes the second-order bound is simply given by

$$\Delta_2 = \tfrac{1}{2}\Delta_1^2 . \quad (10)$$

For a system invariant under a time reversal, Spruch proved this result for the amplitudes corresponding to remaining in the initial state, and suggested that it might be true for amplitudes corresponding to transition from state $n$ of one arrangement channel to state $n$ of another arrangement channel; i.e., a rearrangement reaction from state $n$. This can be easily demonstrated; one can choose trial wave functions such that[1]

$$\chi_{n2R} = K\chi_{n1}(-t) ,$$

where $K$ is an antiunitary time reversal operator,[6] and so

$$\Delta_2 = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \, \|D(\chi_{n1})\| \int_t^{\infty} dt' \|D(\chi_{n2R})\| = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \, \|D(\chi_{n1})\| \int_{-\infty}^{-t} dt' \|D(\chi_{n1})\| . \quad (11)$$

Equation (10) follows by considering the symmetry of the double time integration.

It should be noted that implicit in the derivation of the variational bounds in this work is the assumption that the trial wave function belongs to the class of functions that have the same asymptotic form as the exact wave function: i.e., time-independent linear combinations of the dynamical states of the system.[1] If this is not so, then Eq. (1) cannot be obtained, and the bounds, if calculated, will be infinite, since the norm of the deviation vector will not vanish as $|t| \to \infty$. This requirement therefore limits the usefulness of these variational bounds to those systems for which the exact ionic and atomic wave functions are available: one-electron systems such as $H^+$-H or $He^{++}$-H, or those multielectron systems that can be approximated by one-electron model systems.[7]

*Partial support under Grant No. AT-464 from the Robert A. Welch Foundation is gratefully acknowledged.

[1]D. Storm, Phys. Rev. A 8, 1789 (1973).
[2]L. Aspinall and I. C. Percival, J. Phys. B 1, 589 (1968).
[3]L. Spruch, in *Lectures in Theoretical Physics—Atomic Collisions*, edited by S. Geltman, K. T. Mahanthappa, and W. E. Brittin (Gordon and Breach, New York, 1968), XIC, p. 77–87.
[4]T. A. Green, Proc. Phys. Soc. 86, 1017 (1965).
[5]R. Shakeshaft, J. Macek, and E. Gerjuoy, J. Phys. B 6, 794 (1973).
[6]A. Messiah, *Quantum Mechanics* (Wiley, New York, 1966), Vol. II, Ch. XV.
[7]D. Storm and D. Rapp, J. Chem. Phys. 57, 4278 (1972).