Comment on the mean-square deviation formula for autoionizing states

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We offer a derivation of the mean-square deviation formula, recently employed in variational calculations of autoionizing states, from a time-dependent point of view.

In recent papers[1-4] the formula

$$\delta \Delta = \delta \langle (H - \langle H \rangle)^2 \rangle = 0 \tag{1}$$

has formed the basis for variational calculations of autoionizing states and energies. We would like to offer a conceptually simple and meaningful derivation of the above formula.

In Refs. 5 and 6 we adopted a time-dependent point of view for understanding and computing the properties of autoionizing states. Further work along these lines has been completed recently.[7-9] The autoionizing states are treated as nonstationary states satisfying

$$\psi(t) = e^{-(i/\hbar)Ht} |\psi_0\rangle \tag{2}$$

with

$$|\psi_0\rangle \equiv |\psi(t=0)\rangle, \tag{3}$$

$$H_0 |\psi_0\rangle \equiv (H - V) |\psi_0\rangle = E_0 |\psi_0\rangle. \tag{4}$$

Physically the state $|\psi_0\rangle$ is defined uniquely. It is the initial, localized state which describes all the interactions at $t = 0$. Mathematically, it can be represented by an exact square-integrable wave function satisfying the Schrödinger differential equation with asymptotically vanishing boundary conditions. It is related to the Gamow complex wave functions with complex eigenvalues in the second Riemann sheet, by analytic continuation.[9]

The very notion of a decaying state implies the following limit:

$$|\psi(t)\rangle \to |\psi_0\rangle, \quad \text{as } t \to 0. \tag{5}$$

For a stationary state, the expression

$$\Delta = \langle (H - \langle H \rangle)^2 \rangle = 0. \tag{6}$$

Thus, one intuitively would expect that, when the limit of Eq. (5) is taken,

$$\Delta(\psi_0) \equiv \langle \psi_0 | (H - \langle H \rangle)^2 | \psi_0 \rangle = \min. \tag{7}$$

This can be seen from the following considera-tion: Let

$$u(t) \equiv \psi(t) - \psi_0(t), \tag{8}$$

where $\psi(t)$ satisfies Eq. (2) and

$$\psi_0(t) = e^{-(i/\hbar)H_0 t} |\psi_0\rangle. \tag{9}$$

We now consider an infinitesimal unitary transformation such that

$$\left\| \lim_{t \to 0} u(t) \right\| = \min \tag{10}$$

or

$$\left\| \lim_{t \to 0} (e^{-i/\hbar Ht} - e^{-i/\hbar H_0 t}) |\psi_0\rangle \right\| = \min. \tag{11}$$

The physically meaningful and mathematically correct limit is then obtained by allowing

$$e^{\pm(i/\hbar)Ht} \underset{t \to 0}{\sim} 1 \pm (i/\hbar)Ht,$$
$$e^{\pm(i/\hbar)H_0 t} \underset{t \to 0}{\sim} 1 \pm (i/\hbar)H_0 t, \tag{12}$$

so that H and H_0 are, as required, the generators of the canonical transformation.

Substitution of Eqs. (12) into Eq. (11) yields the desired relationship, Eq. (7), and from it

$$\delta \Delta(\psi_0) = \delta(\langle \psi_0 | H^2 | \psi_0 \rangle - \langle \psi_0 | H | \psi_0 \rangle^2) = 0. \tag{13}$$

Equation (13) employs square-integrable wave functions.

Applications of this formula to He autoionizing states and to the Stark effect from different points of view have been presented in Refs. 1, 3, and 4. Also in Ref. 3, a derivation of Eq. (13) is presented by requiring that the variation of the decay function with respect to ψ_0 is zero [Eq. (4) of Ref. 3].

Note added in proof. In Ref. 10, a new variational principle is presented which employs complex functions and matrix elements of H^2 and yields both

the energy and the width of resonances. In the limiting case where the complex parameters or coordinates of the basis functions become real, this principle reduces to Eq. (13).

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