Generalized recurrence relation for the calculation of two-center matrix elements

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As a novel application of the hypervirial theorem, a new recursion relation for the calculation of any operator two-center integral, in the most general case of arbitrary potential eigenfunctions, is presented. The proposed formula, in addition to reducing properly to the recurrence relation for the calculation of one-center matrix elements that come from the second hypervirial theorem, allows us to obtain a generalization of the Ta-You Wu equation for the calculation of Franck-Condon factors.

I. INTRODUCTION

Since 1960, when Hirschfelder[1] proposed the hypervirial relations

$$\langle m \mid [H,f(x)] \mid n \rangle = (E_m - E_n)\langle m \mid f(x) \mid n \rangle \quad (1.1)$$

and

$$\langle m \mid [H,[H,f(x)]] \mid n \rangle = (E_m - E_n)^2 \langle m \mid f(x) \mid n \rangle , \quad (1.2)$$

numerous efforts have been dedicated to deriving relationships between quantum-mechanical matrix elements. In fact, from the second hypervirial theorem [Eq. (1.2)], the exact generalized recurrence relation for the calculation of $f(x)$ matrix elements as a function of eigenenergies E_m, E_n for any one-dimensional potential $V(x)$ (Refs. 2 and 3),

$$(E_m - E_n)^2 \langle m \mid f(x) \mid n \rangle = -\alpha^2 \left\langle m \left| \frac{d^4 f(x)}{dx^4} \right| n \right\rangle - 2\alpha(E_m + E_n) \left\langle m \left| \frac{d^2 f(x)}{dx^2} \right| n \right\rangle + 4\alpha \left\langle m \left| \frac{d^2 f(x)}{dx^2} V(x) \right| n \right\rangle + 2\alpha \left\langle m \left| \frac{df(x)}{dx} \frac{dV(x)}{dx} \right| n \right\rangle , \quad (1.3)$$

where $\alpha = \hbar^2/2\mu$, has been successfully employed in the literature and different particular cases have been reported.[4-12] However, as far as we know, the power of hypervirial methods has not been exploited to obtain a recurrence relation for the calculation of two-center matrix elements.[13] With this purpose in mind, and by using a hypervirial-like theorem with commutator algebra, Sec. II is devoted to the determination of a generalized recurrence relation for matrix elements of an arbitrary function between states represented by eigenfunctions corresponding to different potential functions. The equation thus obtained contains as a particular case the exact recurrence relation for the calculation of one-center integrals as specified by Eq. (1.3).

II. GENERALIZED RECURRENCE RELATION FOR TWO-CENTER INTEGRALS

Consider two arbitrary potentials $V(x_G) = V_G$ and $V(x_E) = V_E$ with the respective one-dimensional Hamiltonians

$$H_G = -\alpha_G \frac{d^2}{dx_G^2} + V_G \quad (2.1)$$

and

$$H_E = -\alpha_E \frac{d^2}{dx_E^2} + V_E \quad (2.2)$$

with the properties

$${}_G\langle m \mid H_G = E_G^m \, {}_G\langle m \mid , \quad H_E \mid n \rangle_E = E_E^n \mid n \rangle_E , \quad (2.3)$$

where $\alpha_{G(E)} = \hbar^2/2\mu_{G(E)}$ and the eigenenergies $E_{G(E)}^{m(n)}$, mass $\mu_{G(E)}$, and potentials $V_{G(E)}$ parameters are assumed to be known; G and E refer to the ground ${}_G\langle \mid$ and excited $\mid \rangle_E$ states. Without loss of generality we can assume that the two potentials are displaced from their respective equilibrium positions according to $x_G - x_E = l$.

In such cases

$$H_G=\frac{\alpha_G}{\alpha_E}(H_E-V_E)+V_G \tag{2.4}$$

and

$$H_E=\frac{\alpha_E}{\alpha_G}(H_G-V_G)+V_E \ . \tag{2.5}$$

Then, for a $f(x_E)=f_E$ function such that

$$[V_G,f_E]=[V_E,f_E]=0 \ ,$$

a hypervirial-like theorem commutator algebra procedure leads to

$$[H_E,f_E]=\frac{\alpha_E}{\alpha_G}H_Gf_E-\frac{\alpha_E}{\alpha_G}V_Gf_E+V_Ef_E-f_EH_E \tag{2.6}$$

and

$$[H_E,f_E]=-\alpha_E\left[\frac{d^2f_E}{dx_E^2}+2\frac{df_E}{dx_E}\frac{d}{dx}\right] , \tag{2.7}$$

where $(d/dx)=(d/dx_G)=(d/dx_E)$. In order to avoid the differential operator (d/dx) it is convenient to solve the commutator $[H_E,(df_E/dx_E)(d/dx)]$. It is given by

$$\left[H_E,\frac{df_E}{dx_E}\frac{d}{dx}\right]=-\frac{1}{2}\frac{\alpha_E}{\alpha_G}V_G\frac{d^2f_E}{dx_E^2}-\frac{3}{2}V_E\frac{d^2f_E}{dx_E^2}+\frac{1}{2}\alpha_E\frac{d^4f_E}{dx_E^4}+\frac{3}{2}\frac{d^2f_E}{dx_E^2}H_E+\frac{1}{2}\frac{\alpha_E}{\alpha_G}H_G\frac{d^2f_E}{dx_E^2}-\frac{df_E}{dx_E}\frac{dV_E}{dx_E} \tag{2.8}$$

and

$$\begin{aligned}\left[H_E,\frac{df_E}{dx_E}\frac{d}{dx}\right]=&-\frac{1}{2}\frac{1}{\alpha_G}H_G\left[V_E-\frac{\alpha_E}{\alpha_G}V_G\right]f_E-\frac{1}{2}\frac{\alpha_E}{\alpha_G}H_G\frac{d^2f_E}{dx_E^2}+\frac{1}{\alpha_G}H_Gf_EH_E-\frac{1}{2}\frac{\alpha_E}{\alpha_G^2}H_G^2f_E\\&+\frac{1}{\alpha_E}\left[V_E-\frac{\alpha_E}{\alpha_G}V_G\right]f_EH_E-\frac{1}{2}\left[V_E-\frac{\alpha_E}{\alpha_G}V_G\right]\frac{d^2f_E}{dx_E^2}+\frac{1}{2}\frac{d^2f_E}{dx_E^2}H_E-\frac{1}{2}\frac{1}{\alpha_E}f_EH_E^2\\&-\frac{1}{2}\frac{1}{\alpha_E}\sum_k E_E^k\left[E_E^k-\frac{\alpha_E}{\alpha_G}H_G\right]|k\rangle_E\,{}_E\langle k|f_E \ .\end{aligned} \tag{2.9}$$

Thus the above two identities along with the properties specified by Eqs. (2.3) allow us to obtain

$$\begin{aligned}&\left[\frac{\alpha_E}{\alpha_G^2}(E_G^m)^2+\frac{1}{\alpha_E}(E_E^n)^2-\frac{2}{\alpha_G}E_G^mE_E^n\right]{}_G\langle m|f_E|n\rangle_E\\&=-\left[\frac{1}{\alpha_G}E_G^m-\frac{2}{\alpha_E}E_E^n\right]{}_G\left\langle m\left|\left[V_E-\frac{\alpha_E}{\alpha_G}V_G\right]f_E\right|n\right\rangle_E-2\left[\frac{\alpha_E}{\alpha_G}E_G^m+E_E^n\right]{}_G\left\langle m\left|\frac{d^2f_E}{dx_E^2}\right|n\right\rangle_E\\&\quad+2\,{}_G\left\langle m\left|\left[V_E+\frac{\alpha_E}{\alpha_G}V_G\right]\frac{d^2f_E}{dx_E^2}\right|n\right\rangle_E-\alpha_E\,{}_G\left\langle m\left|\frac{d^4f_E}{dx_E^4}\right|n\right\rangle_E+2\,{}_G\left\langle m\left|\frac{df_E}{dx_E}\frac{dV_E}{dx_E}\right|n\right\rangle_E\\&\quad-\frac{1}{\alpha_E}\sum_k E_E^k\left[E_E^k-\frac{\alpha_E}{\alpha_G}E_G^m\right]{}_G\langle m|k\rangle_E\,{}_E\langle k|f_E|n\rangle_E \ .\end{aligned} \tag{2.10}$$

This equation is an exact recurrence relation generalized for the calculation of $f(x)$ two-center matrix elements as a function of eigenenergies for any $V(x)$. It contains several particular cases: When $G=E$ one recovers the corresponding formula for the calculation of one-center integrals, Eq. (1.3), that comes from the second hypervirial theorem.

For $f_E=\text{const}$ Eq. (2.10) reduces to

$$\left[\frac{\alpha_E}{\alpha_G}E_G^m-E_E^n\right]{}_G\langle m|n\rangle_E=\frac{\alpha_E}{\alpha_G}\,{}_G\langle m|V_G|n\rangle_E-{}_G\langle m|V_E|n\rangle_E \ . \tag{2.11}$$

This relation, useful for the calculation of Franck-Condon factors, is a generalization of the Ta-You Wu[14] formula and can also be obtained directly from Eqs. (2.6) and (2.7).[15]

III. DISCUSSION

As a novel application of the hypervirial theorem, we have obtained a new recurrence relation for the calculation of two-center matrix elements. The proposed formula is given in the most general case for any potential as well as $f(x)$. As expected, our formula contains as a particular case the corresponding generalized recurrence relation for the calculation of one-center integrals that has been successfully used in the literature for many years. On the other hand, from Eq. (2.10), we have shown that the Ta-You Wu formula, for the calculation of overlap integrals in the particular case of $\mu_G = \mu_E$, has been generalized to Eq. (2.11). In short, the proposed formula for the calculation of two-center integrals should be used along with the corresponding equation for the evaluation of ${}_E\langle k \mid f_E \mid n \rangle_E$ one-center integrals, Eq. (1.3), and the one for the overlap integrals ${}_G\langle m \mid k \rangle_E$, Eq. (2.11), which closes the loop.

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