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Transition moments for linear potentials

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Abstract. A new method based on hypervirial relationships is used to calculate transition moments for linear potentials of bounded systems, generalising previous results. The deduced equations are applied to the model of an electron in a finite unidimensional crystal under the influence of an external uniform electric field.

1. Introduction

The linear potential possesses a marked importance in physics, because it enables us to study several phenomena of great interest. Among them, we can mention the properties of an electron in a finite-range constant electric field (Rabinovitch and Zak 1971), disordered systems (Lukes *et al* 1976) and narrow boson resonances (Harrington *et al* 1975). Because of this, some authors have paid special attention to the evaluation of matrix elements of coordinate powers in a basis set of Airy functions (A_i) (Ferreira and Alcarás 1975, Aguilera-Navarro *et al* 1980). In both cases, only the regular Airy functions were used, because the variable could attain any value within the range $[0, \infty)$. As far as we know, up to now nobody has investigated which are the modifications (if any) for the expressions of the transition moments given previously (Ferreira and Alcarás 1975, Aguilera-Navarro *et al* 1980) when the range of the variable is restricted to be a finite interval. This situation is not an artificial one, because it must be considered in an explicit fashion in certain cases (Lukes *et al* 1976, Rabinovitch and Zak 1971).

Recently, we have presented a new method which permits one to obtain in an analytical form the perturbation corrections for some bounded systems (Fernández and Castro 1981a–h). By means of this procedure, which is based on the hypervirial theorems, we could analyse in a very satisfactory way the unidimensional harmonic oscillator model for different boundary conditions, the multidimensional isotropic bounded oscillator, the hydrogen atom inside impenetrable spherical and paraboloidal surfaces, and a unidimensional bounded system subjected to a linear potential.

The purpose of this communication is to apply the hypervirial relationships (HR), diagonal (DHR) as well as off-diagonal (ODHR), in order to obtain matrix elements of a more general character than those deduced formerly by Ferreira and Alcaras (1975) and Aguilera-Navarro *et al* (1980). The methodology used here has been already employed for calculating transition moments with a basis set of Bessel functions (Fernández *et al* 1981). It proved to be a very efficient procedure and particularly

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easy to apply. One of the most important and attractive features of the HR consists in the possibility of dealing with any boundary condition (BC).

The plan of this paper is as follows: in § 2 we present briefly some general properties of the solutions of the Schrödinger equation with a linear potential. Section 3 is devoted to deducing the HR from which the matrix elements of the coordinate powers will be obtained when the range of the coordinate is finite, say $[0, x_0]$, and for Dirichlet boundary conditions (DBC). In the limit $x_0 \to \infty$, our results coincide with those previously given by Ferreira and Alcarás (1975) and Aguilera-Navarro *et al* (1980), which can be considered as particular cases of ours. The equations obtained in this section are applied in § 4 to calculate some transition moments for the model of an electron which is moving in a finite one-dimensional empty crystal under the influence of a uniform electric field. Finally, in § 5 we display some possible extensions of the method which enables us to discuss more complex cases.

2. One-dimensional Schrödinger equation with a linear potential

Let us consider the Schrödinger equation

$$H\phi = E\phi, \tag{1}$$

$$H = -\tfrac{1}{2}\,\mathrm{d}^2/\mathrm{d}x^2 + gx, \tag{2}$$

where the wavefunction ϕ is subjected to the BC

$$\phi(0) = \phi(x_0) = 0. \tag{3}$$

Defining the new variable y by

$$y = (2g)^{1/3}x - e, \qquad e = 2^{1/3}g^{-2/3}E, \tag{4}$$

equation (1) is transformed into the Airy differential equation

$$f''(y) - yf(y) = 0, \qquad f(y) = \phi[(2g)^{-1/3}\,y + E/g]. \tag{5}$$

The eigenvalues are determined via the BC (3),

$$D_e = \begin{vmatrix} A_i(y_{0n}) & B_i(y_{0n}) \\ A_i(-e_n) & B_i(-e_n) \end{vmatrix} = 0, \qquad y_{0n} = (2g)^{1/3}x_0 - e_n, \tag{6}$$

where e_n are the roots of the determinant D_e, $A_i(y)$ is the regular Airy function and $B_i(y)$ is the non-regular Airy function (Abramowitz and Stegun 1965). The eigenfunctions associated with equation (1) that fulfil the BC (3) have the following form:

$$\phi_n(x) = N_n\left(A_i[(2g)^{1/3}x - e_n] - \frac{A_i(-e_n)}{B_i(-e_n)}\,B_i[(2g)^{1/3}x - e_n]\right). \tag{7}$$

According to the properties of the functions $A_i(y)$ and $B_i(y)$, the condition

$$\lim_{x_0 \to \infty} \phi_n(x) = N'_n\,A_i[(2g)^{1/3}x + a_n] \tag{8}$$

is satisfied, with a_n the nth zero of $A_i(y)$.

When x_0 is large enough, the asymptotic behaviour of the Airy functions (Abramowitz and Stegun 1965) allows us to deduce at once that (Aguilera-Navarro *et al* 1981)

$$-e_n \cong a_n + (B_i(a_n)/2A_i'(a_n))\,\mathrm{e}^{-2z}, \qquad z = \tfrac{2}{3}[(2g)^{1/3}x_0 + a_n]^{3/2}, \tag{9}$$

$$\phi_n \cong N_n\{A_i[(2g)^{1/3}x - e_n] - \tfrac{1}{2}\mathrm{e}^{-2z}\,B_i[(2g)^{1/3}x - e_n]\}. \tag{10}$$

3. Matrix elements

The solutions $\phi_n(x)$ of the Schrödinger equation

$$H\phi_n = E_n\phi_n, \qquad \langle\phi_n|\phi_m\rangle = \delta_{nm}, \tag{11}$$

$$H = -\tfrac{1}{2}\mathrm{d}^2/\mathrm{d}x^2 + V(x), \qquad x \in [a, b], \tag{12}$$

subject to the BC

$$\phi_n(a) = A\phi_n'(a), \qquad \phi_n(b) = B\phi_n'(b), \tag{13}$$

must satisfy the following HR (Fernández and Castro 1981a–h);

$$\langle n|[H, W]|m\rangle = (E_n - E_m)\langle n|W|m\rangle + R_{nm}(W) \tag{14}$$

for any arbitrary linear operator W, and with

$$R_{nm}(W) = \tfrac{1}{2}[\phi_n'(x)W\phi_m(x) - \phi_n(x)(W\phi_m)'(x)]_a^b. \tag{15}$$

From equation (14) we deduce immediately the equation

$$\tfrac{1}{4}\langle n|f'''|m\rangle + (E_n + E_m)\langle n|f'|m\rangle - 2\langle n|f'V|m\rangle - \langle n|fV'|m\rangle + (E_n - E_m)^2\langle n|F|m\rangle = R_{nm}(fD) - (E_n - E_m)R_{nm}(F) - \tfrac{1}{2}R_{nm}(f') \tag{16}$$

for any differentiable function $F(x)$ such that $F'(x) = f(x)$, and with $D \equiv \mathrm{d}/\mathrm{d}x$. When the eigenfunctions satisfy the DBC ($A = B = 0$ in equation (13))

$$\phi_n(a) = \phi_n(b) = 0 \tag{17}$$

and $f(x)$ possesses the simple expression

$$f(x) = x^N \tag{18}$$

then equation (16) is transformed into

$$\tfrac{1}{4}N(N-1)(N-2)Q_{nm}^{N-3} + N(E_n + E_m)Q_{nm}^{N-1} - 2N\langle n|x^{N-1}V|m\rangle - \langle n|x^NV'|m\rangle + \frac{(E_n - E_m)^2}{N+1}Q_{nm}^{N+1} = R_{nm}(x^ND) \tag{19}$$

where

$$Q_{nm}^N = \langle n|x^N|m\rangle. \tag{20}$$

When

$$V(x) = gx \tag{21}$$

and $a = 0$, $b \equiv x_0$, then equation (19) yields a recursion relationship which enables us to calculate the whole set of transition moments Q_{nm}^N:

$$\tfrac{1}{4}N(N-1)(N-2)Q_{nm}^{N-3} + N(E_n + E_m)Q_{nm}^{N-1} - (2N+1)gQ_{nm}^N + \frac{(E_n - E_m)^2}{N+1}Q^{N+1} = R_{nm}(x^ND), \tag{22}$$

$$R_{nm}(D)=\tfrac{1}{2}[\phi'_n(x_0)\phi'_m(x_0)-\phi'_n(0)\phi'_m(0)],$$

$$R_{nm}(x^N D)=\tfrac{1}{2}x_0^N\phi'_n(x_0)\phi'_m(x_0), \qquad N>0. \tag{23}$$

Starting from $N=0$, the successive assignment of values to N allows us to obtain all the integrals Q^N_{nm}. For $N=0$ and $N=1$, the results are

$$\phi'_n(0)^2-\phi'_n(x_0)^2=2g \qquad \text{(normalisation condition)}, \tag{24}$$

$$Q^1_{nm}=\tfrac{1}{2}(\phi'_n(x_0)\phi'_m(x_0)-\phi'_n(0)\phi'_m(0))(E_n-E_m)^{-2}, \qquad n\neq m, \tag{25}$$

$$Q^1_{nn}=(1/3g)[2E_n-\tfrac{1}{2}x_0(\phi'_n(0)^2-2g)], \tag{26}$$

$$Q^2_{nm}=2[3gQ^1_{nm}+\tfrac{1}{2}x_0(\phi'_n(x_0)\phi'_m(x_0))](E_n-E_m)^{-2}, \qquad n\neq m, \tag{27}$$

where

$$\phi'_n(0)=N_n(2g)^{1/3}\left(A'_i(-e_n)-\frac{A_i(-e_n)}{B_i(-e_n)}B'_i(-e_n)\right). \tag{28}$$

The high-order transition moments are deduced in a similar fashion. When $x_0\to\infty$, our results tend to those formerly presented by Ferreira and Alcarás (1975), and Aguilera-Navarro *et al* (1980), i.e.

$$N_n=(2g)^{1/6}/A'_i(a_n), \tag{29}$$

$$R_{nm}(D)=-g, \qquad R_{nm}(x^N D)=0, \qquad N>0, \tag{30}$$

$$Q^1_{nm}=-g(E_n-E_m)^{-2}, \qquad n\neq m, \tag{31}$$

$$Q^1_{nn}=2E_n/3g, \tag{32}$$

$$Q^2_{nm}=-6g^2(E_n-E_m)^{-4}, \qquad n\neq m, \tag{33}$$

$$E_n=-g^{2/3}a_n/2^{1/3}. \tag{34}$$

When x_0 is large enough, we can replace equations (9)–(10) in (22)–(28) with the purpose of determining the asymptotic behaviour of the transition moments.

4. Electron in a finite unidimensional crystal under the influence of an external electric field. The empty crystal model

The eigenstates of an electron of mass m and electric charge $-e$ which is moving in an empty crystal of length L under an applied electric field of strength F, are given by the following Schrödinger equation:

$$-(\hbar^2/2m)\Psi''(q)+fq\Psi(q)=E'\Psi(q), \tag{35}$$

$$\Psi(-L/2)=\Psi(L/2)=0 \tag{36}$$

where

$$f=eF. \tag{37}$$

This model was used by Rabinovitch and Zak (1971) to study the boundary effects on the electronic states, bearing in mind that in physical reality the crystal's range and the range of the electric field are finite. Also Lukes *et al* (1976) used this model to discuss the density of states for disordered systems in the presence of an electric field.

In this section we apply the preceding formal results to show the variation of the transition moments as a function of the crystal length L. Making the change of variable

$$x=(mf\hbar^{-2})^{1/3}\,(q+L/2), \tag{38}$$

equations (35)–(36) are transformed to

$$-\tfrac{1}{2}\phi''(x)+x\phi(x)=E\phi(x), \qquad E=(m\hbar^{-2}f^{-2})^{1/3}E'+(mf\hbar^{-2})^{1/3}L/2, \tag{39}$$

$$\phi(0)=\phi(x_0)=0, \qquad x_0=(mf\hbar^{-2})^{1/3}L. \tag{40}$$

These equations coincide with equations (1)–(3) when $g=1$. In order to calculate the transition moments, it is convenient to modify the normalisation condition (24) as follows:

$$\phi'_n(0)^2+2\,\partial E_n/\partial x_0=2g. \tag{41}$$

We have applied the result (Fernández and Castro 1981a)

$$\partial E_n/\partial x_0=-\tfrac{1}{2}\phi'_n(x_0)^2 \tag{42}$$

to deduce equation (41).

Choosing the sign of the functions $\phi_n(x)$ in such a way that $\phi'_n(x_0)>0$, we obtain

$$\phi'_n(0)=(-1)^{n-1}(2g-2\,\partial E_n/\partial x_0)^{1/2} \tag{43}$$

where $n-1$ is the number of zeros of $\phi_n(x)$ in $(0, x_0)$. Then, we need only to know $E_n(x_0)$ for the purpose of computing the transition moments. From the HPM, we have obtained (Fernández and Castro 1981h) an analytical expression for the eigenvalues of (39)–(40) corrected in a perturbative manner up to the fourth order:

$$E_n \cong C_n x_0^{-2}+0.5x_0+[(48C_n)^{-1}-5(32\,C_n^2)^{-1}]x_0^4$$
$$+[(2304\,C_n^3)^{-1}-70(1536\,C_n^4)^{-1}+55(256\,C_n^5)^{-1}]x_0^{10} \tag{44}$$

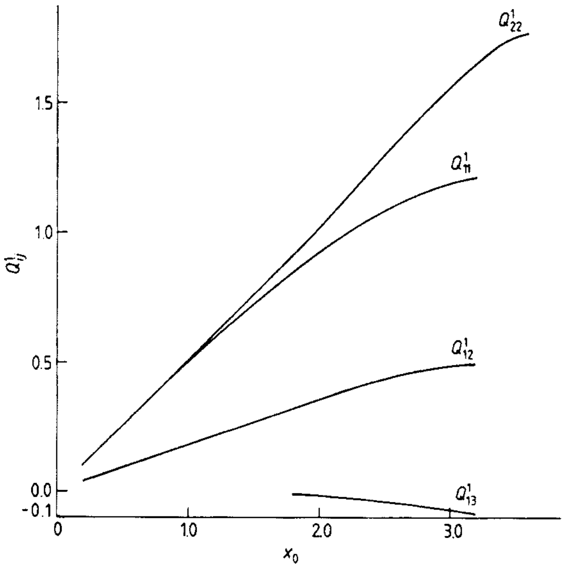

Figure 1. First transition moments Q^1_{ij} for an electron in an empty crystal in the presence of a uniform electric field.

where

$$C_n = 0.5\, n^2\pi^2. \tag{45}$$

Due to the fact that this formula gives very good results for the ground state when $x_0 \leqslant 3.2$, and for the first excited state when $x_0 \leqslant 3.5$, we have calculated the transition moments in such a range of x_0 values. We display in figure 1 the variation of transition moments Q^1_{11}, Q^1_{22}, Q^1_{12} and Q^1_{13} as a function of x_0.

5. Conclusions

The study of the three-dimensional Schrödinger equation for a linear radial potential (Harrington *et al* 1975, Ferreira and Alcarás 1975) requires us to consider the unidimensional eigenvalue equations (11)–(12) for a potential function

$$V(x) = gx + t/2x^2. \tag{46}$$

When $t = 0$, the results of the preceding sections are wholly applicable. But for $t \neq 0$ equation (19) is transformed to

$$(N-1)[0.25N(N-2)-t]Q^{N-3}_{nm} + N(E_n+E_m)Q^{N-1}_{nm} - (2N+1)gQ^N_{nm} + \frac{(E_n-E_m)^2}{N+1}Q^{N+1}_{nm} = R_{nm}(x^N D). \tag{47}$$

Although equation (47) is slightly different with respect to equation (22), the new term complicates the equation in such a way that now it is not so easy to calculate the matrix elements Q^N_{nm} as previously. For $N = 0$ and $N = 1$, the following results are deduced:

$$tQ^{-3}_{nn} = g + R_{nn}(D), \tag{48}$$

$$tQ^{-3}_{nm} + (E_n - E_m)^2 Q^1_{nm} = R_{nm}(D), \qquad n \neq m, \tag{49}$$

$$2E_n - 3gQ^1_{nn} = R_{nn}(xD), \tag{50}$$

$$0.5Q^2_{nm}(E_n - E_m)^2 - 3gQ^1_{nm} = R_{nm}(xD). \tag{51}$$

Although the presence of negative powers does not allow us to make a similar calculation to that presented in § 2, these equations are of a marked usefulness because they relate all the moments with a reduced number of quantities.

Finally, we deem it appropriate to point out that the treatment presented in this communication is not restricted to DBC, but is equally suitable for any BC with the general form (13). In particular, it is important to note that von Neumann BC are especially favoured owing to the fact that the zeros of $A_i'(y)$ and $B_i'(y)$ are tabulated (Abramowitz and Stegun 1965).

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