UPPER AND LOWER BOUNDS FOR THE SCHRÖDINGER-EQUATION EIGENVALUES

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Received 18 April 1986; accepted for publication 14 May 1986

The calculation of upper and lower bounds for the Schrödinger-equation eigenvalues from moment recurrence relations is reviewed. A previous algorithm originally developed to approach the ground state is shown to apply also to the first excited state of parity-invariant systems. Alternative recurrence relations based on the hypervirial theorems are proposed that yield bounds for all the states simultaneously.

The calculation of upper and lower bounds for the eigenvalues of the Schrödinger equation is of utmost importance in quantum mechanics. Recently Handy and Bessis [1] have shown that, in some cases, simultaneous upper and lower bounds can be obtained from moment problems. Their method is based on the Hankel–Hadamard determinant inequalities that express the necessary and sufficient conditions for a sequence of numbers $\mu_1,\mu_2,\ldots$ to be the Stieltjes moments of a nonnegative function (say $\phi(x)$) [2]. The inequalities are

$$H_k^0 > 0, \quad H_k^1 > 0, \tag{1}$$

where $H_k^m = \det|B|$ and $B_{ij} = \mu_{m+i+j-2}$, $i, j = 1, 2, \ldots, k+1$. The Stieltjes moments are defined as

$$\mu_n = \int_0^\infty x^n \phi(x)\, \mathrm{d}x. \tag{2}$$

The ground-state wavefunction $\psi(x)$ (for the sake of simplicity we consider one-dimensional problems) of a bosonic system is nonnegative and all its hamburger moments

$$\mu_n = \int_{-\infty}^\infty x^n \psi(x)\, \mathrm{d}x \tag{3}$$

exist. In this case, one can easily prove that $H_k^{2m} > 0$ for all m and k [2].

If the system is parity invariant, the odd moments vanish and we have a Stieltjes moment problem with $\phi(x) = x^{-1/2}\psi(x^{1/2})$ [1]. Handy and Bessis [1] applied their method (named HBM from now on) to the ground state of several parity-invariant one-dimensional bosonic systems. Although they argued that the HBM can also be applied to excited states or to fermionic problems, they did not show any example. However, it can be easily proved that the HBM can be applied, almost without modification, to the first excited state of a parity-invariant system. In fact, in this case we have a Stieltjes moment problem with $\phi(x) = \psi(x^{1/2})$ provided that the wavefunction is chosen so that $\psi(x) > 0$ for $x > 0$. This can be accomplished by setting $\mu_0 > 0$ in the moment recurrence relation. Since the calculation scheme is similar to that in ref. [1], we deem it unnecessary to show an example here.

Let us now consider a general way of obtaining simple moment recurrence relations. Suppose that $\psi(\boldsymbol{x})$, where $\boldsymbol{x} = (x_1, x_2, \ldots, x_f)$, is a solution of the differential equation

$$P(\boldsymbol{x})\Delta\psi(\boldsymbol{x}) + Q(\boldsymbol{x})\psi(\boldsymbol{x}) = 0, \tag{4}$$

where Δ is the laplacian operator and P and Q are polynomial functions of the coordinates. If we multiply eq. (4) by a function $\Phi(x)$ so that $\Phi\psi$ and its first derivatives vanish at the boundaries, we obtain (after integrating by parts)

$$\int \psi \Delta(P\Phi)\, \mathrm{d}x + \int Q\Phi\psi\, \mathrm{d}x = 0. \tag{5}$$

A proper choice of $\Phi(x)$ transforms eq. (5) into a moment recurrence relation. For example, if $\Phi(x)$ obeys

$$\Delta(P\Phi) + U\Phi = 0, \tag{6}$$

where U is a polynomial function of the coordinates, then eq. (5) becomes

$$\int (Q - U)\Phi\psi\, \mathrm{d}x = 0. \tag{7}$$

This argument is a generalization of the procedure that Handy and Bessis used to avoid the missing moments [1]. Eqs. (6) and (7) are also useful in perturbation theory [3] and to generate the simplest moment recurrence relations. Let us briefly illustrate the latter point by means of the Schrödinger equation for the anharmonic oscillator

$$-\psi'' + (x^2 + \lambda x^4)\psi = E\psi. \tag{8}$$

The choice $\Phi = x^n \exp(-\alpha x^2)$ yields

$$-n(n-1)\mu_{n-2} + (1 - 4\alpha^2)\mu_{n+2} + \lambda\mu_{n+4} = [E - 2\alpha(2n+1)]\mu_n. \tag{9}$$

If $\alpha = 0$, we are led to the four-term recurrence relation shown in ref. [1], but a simpler one is obtained when $\alpha = 1/2$ since the coefficient of μ_{n+2} vanishes.

Handy and Bessis [1] suggested that their method can be applied to excited states and fermionic systems through a proper analysis of the wavefunction nodes. We point out that this would be unnecessary if we had a recurrence relation for the moments of ψ^2. Such a relation can, in fact, be obtained for some one-dimensional problems by means of the hypervirial theorems [4–6]. To see this, suppose that the Schrödinger equation can be written

$$P(x)\psi''(x) + Q(x)\psi'(x) + R(x)\psi(x) = 0, \tag{10}$$

where P, Q and R are polynomial functions of the coordinate. It is understood that either $-\infty < x < \infty$ and $\psi(x)$ vanishes at infinity or $a < x < b$ and both $P(x)$ and $\psi(x)$ vanish at the end points of the interval.

If eq. (10) is first multiplied by $f(x)\psi(x)$ and then by $F(x)\psi'(x)$ and one of the resulting equations is subtracted from the other, we obtain (after integrating by parts)

$$\tfrac{1}{2}\int (fP)''\psi^2\, \mathrm{d}x + \tfrac{1}{2}\int (FR)'\psi^2\, \mathrm{d}x + \int fR\psi^2\, \mathrm{d}x - \tfrac{1}{2}\int (fQ)'\psi^2\, \mathrm{d}x = 0, \tag{11}$$

provided that $f(x)$ and $F(x)$ are related by

$$\tfrac{1}{2}(PF)' - QF - fP = 0. \tag{12}$$

Upon choosing $f = x^n$ ($n = 0, 1, \ldots$), F is found to be a polynomial function of the coordinate and eq. (11) becomes a recurrence relation for the hamburger moments

$$\mu_n = \int_{-\infty}^{\infty} x^n \psi^2\, \mathrm{d}x. \tag{13}$$

Therefore, $H_k^{2m} > 0$ for all the eigenfunctions since ψ^2 is positive definite [2].

As a general rule, the missing-moment problem seems to be more serious in the hypervirial method than in HBM. In what follows, we will consider two quantum-mechanical models which, although trivial, are very useful to illustrate the performance of the hypervirial method because the recurrence relations are free from missing moments.

For the harmonic oscillator, eq. (11) with $P \equiv -1$, $Q \equiv 0$, $R = x^2 - E$ and $f = x^{n-1}$ becomes

$$\mu_{n+1} = nE\mu_{n-1}/(n+1) + n(n-1)(n-2)\mu_{n-3}/4(n+1). \tag{14}$$

A Stieltjes problem is obtained by writing $n = 2p + 1$ and μ_p instead of μ_{2p}. The inequalities (1) with $k = 7$ yield the bounds shown in table 1. Since all the states are treated simultaneously, the

Table 1
Upper and lower bounds (UB and LB, respectively) for the eigenvalues $E_n = 2n+1$ of the harmonic oscillator obtained from $H_7^0 > 0$ and $H_7^1 > 0$.

n	LB	UB
0	0.999980	1.000054
1	2.99520	3.002514
2	4.94884	5.131029

large-determinant inequalities give rise to many energy bounds that have to be analyzed carefully, particularly those corresponding to the excited states.

The next example is the hydrogen atom. The radial part of the Schrödinger equation for this model can be written (atomic units are used)

$$\left[-r^2\partial^2/\partial r^2 + r^2 - 2ur + l(l+1)\right]\psi = 0, \qquad (15)$$

where ψ vanishes at $r = 0$ and infinity and $l = 0, 1, \ldots$ is the angular momentum quantum number. The eigenvalues are $u_n = n = 1, 2, \ldots$, where n is the principal quantum number. With a given value of l, the HBM applies to the state with principal quantum number $n = l+1$ which is the only one with nodeless radial wavefunction. On the other hand, the hypervirial method treats all the states with the same quantum number l simultaneously.

Eq. (11) with $P = -r^2$, $Q \equiv 0$, and $R = l(l+1) + r^2 - 2ur$ leads to

$$\mu_{n+2} = (2n+5)u\mu_{n+1}/(n+3) - \left[l(l+1)(n+2)/(n+3) - (n+1)(n+2)/4\right]\mu_n. \qquad (16)$$

Table 2
Upper and lower bounds (UB and LB, respectively) for the eigenvalues $u_n = n$ of the hydrogen atom obtained from $H_7^1 > 0$.

n	LB	UB
1	0.9784	1.025
2	1.771	

We briefly consider the s states ($l = 0$). Results for this model are not as satisfactory as those for the previous one. Most of the roots of $H_k^0 > 0$ are complex and the real ones do not give useful information. However, the inequalities $H_k^1 > 0$ lead to increasingly tight bounds. Those for $k = 7$ are shown in table 2.

Although present results are not striking, it is clear that the hypervirial moment method provides upper and lower bounds for all the states of one-dimensional systems, and we deem that it may be very useful in checking eigenenergies and moments obtained from other approaches.

One of the authors (F.M.F.) would like to thank the University of Alabama for financial support.

References

[1] C.R. Handy and D. Bessis, Phys. Rev. Lett. 55 (1985) 931.
[2] G.A. Baker, Jr., Essentials of Padé approximants (Academic Press, New York, 1975) ch. 15.
[3] F.M. Fernandez and E.A. Castro, Int. J. Quantum Chem. 26 (1984) 497; 28 (1985) 603.
[4] R.J. Swenson and S.H. Danforth, J. Chem. Phys. 57 (1972) 1734.
[5] J. Killingbeck, Phys. Lett. A 65 (1978) 87.
[6] F.M. Fernandez and E.A. Castro, Match 15 (1984) 133.