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# Energy-Moment Methods in Quantum Mechanics

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Three quantum-mechanical computational techniques based on energy moments, $\mu_k = \int dq \psi^*(q) \mathcal{H}^k \psi(q)$, and semimoments, $\nu_k(q') = [\mathcal{H}^k \psi(q)]_{q=q'}$, are formulated. The $\mu$ method, which employs the $\mu_k$, is connected to the method of moments in probability theory, to the variational method, and to eigenvalue spectroscopy. The $\nu$ and $\lambda$ methods, which employ semimoments, are related to local energy methods using one and several configuration points, respectively. An $N$th-order calculation, requiring $2N$ moments or semimoments, yields $N$ approximate eigenvalues and eigenfunctions. In accordance with a conjectured convergence criterion, exact eigenstates are approached in the limit $N \to \infty$. From quantities obtained in a moments calculation, a lower bound on the ground-state eigenvalue can also be determined using a refinement of Weinstein's criterion. A computational method for generating moments and semimoments is given and the $\mu$ method is applied to the linear harmonic oscillator.

## I. INTRODUCTION

In this paper three quantum-mechanical approximation methods, all closely related to the method of moments,[1] are formulated. The method of moments was developed by mathematicians during the early part of this century mainly for application to continuous probability distributions. In quantum-mechanical applications the fundamental quantities are moments of the Hamiltonian operator

$$\mu_k \equiv \langle \psi(q), \mathcal{H}^k \psi(q) \rangle, \tag{1}$$

where $\psi(q)$ represents an arbitrary state function obeying the same analyticity, symmetry, and boundary conditions as are imposed on the eigenfunctions $\phi_n(q)$ of the Schrödinger equation

$$(\mathcal{H} - \omega_n)\phi_n(q) = 0. \tag{2}$$

In all cases considered here, the moments (1) are represented more explicitly as integrals over the set of configuration variables $q$. But extension to the case of spinor wavefunctions is straightforward. By an $N$th-order calculation is meant one in which the first $2N$ moments $\mu_0, \mu_1, \mu_2, \cdots, \mu_{2N-1}$ are employed, usually resulting in approximations for $N$ energy eigenvalues.

The first systematic application of the method of moments in quantum mechanics is due apparently to Horvay.[2] In calculation of the binding energy of the oxygen nucleus, he found "exceedingly slow" convergence. Halpern,[3] independently, applied the method to the phonon–polaron interaction. A fifth-order calculation proved partially successful. A subsequent application[4] to a problem in static-source meson theory proved unsuccessful, but this was apparently due to the model rather than the method.

More recently, one of us has developed a formalism ("eigenvalue spectroscopy") in which the eigenvalue spectrum is expressed in terms of a Fourier expansion containing energy moments of all orders.[5,6] The moments are generated by the time-evolution operator according to

$$F(t) = \langle \psi(q), \exp(it\mathcal{H})\psi(q) \rangle = \sum_{k=0}^{\infty} \frac{(it)^k}{k!} \mu_k. \tag{3}$$

The function $F(t)$ corresponds to a moment-generating function in probability theory or to a correlation function in the theory of stochastic processes. Comparing (1) with (3), the moments can be formally represented by

$$\mu_k = i^k F^{(k)}(0). \tag{4}$$

This leads to the following expansion for the eigenvalue spectrum:

$$G(\omega) = 2\pi \sum_{k=0}^{\infty} (-1)^k \frac{\mu^{(k)}}{k!} \delta^{(k)}(\omega), \tag{5}$$

where $\delta^{(k)}(\omega)$ represents the $k$th derivative of Dirac's delta function.

## II. GENERAL THEORY

Consider first a quantum system for which the eigenvalue spectrum consists of a finite number of discrete eigenvalues $\omega_0, \omega_1, \cdots, \omega_{N-1}$. An example would be a system of spins subject only to Zeeman excitations. The projection operator

$$P_N(\mathcal{H}) = \prod_{n=0}^{N-1} (\mathcal{H} - \omega_n) \tag{6}$$

then serves to annihilate any state function $\psi(q)$ lying

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[1] The method of moments is treated in many textbooks on mathematical statistics. See, for example, M.G. Kendall, *The Advanced Theory of Statistics* (Charles Griffin and Co., Ltd., London, 1946–1947) 2 Vols. Yu. V. Vorobyev, *Method of Moments in Applied Mathematics* (Gordon and Breach Science Publications, New York, 1965).

[2] G. Horvay, Phys. Rev. **55**, 70 (1939).

[3] F. R. Halpern, Phys. Rev. **107**, 1145 (1957); **109**, 1836 (1958).

[4] F. R. Halpern, Ann. Phys. (N.Y.) **7**, 154 (1959).

[5] S. M. Blinder, Intern. J. Quantum Chem. **1**, 271 (1967).

[6] S. M. Blinder, J. Chem. Phys. **41**, 3412 (1964).

wholly within the eigenfunction space of $\mathcal{H}$, i.e.,

$$P_N(\mathcal{H})\psi(q)\equiv 0. \tag{7}$$

The annihilating operator is evidently an $N$th-order polynomial in $\mathcal{H}$:

$$P_N(\mathcal{H})=a_0^{(N)}+a_1^{(N)}\mathcal{H}+\cdots+a_{N-1}^{(N)}\mathcal{H}^{N-1}+\mathcal{H}^N \tag{8}$$

such that the $N$ roots of

$$P_N(\omega)=a_0^{(N)}+a_1^{(N)}\omega+\cdots+a_{N-1}^{(N)}\omega^{N-1}+\omega^N=0 \tag{9}$$

correspond to the $N$ eigenvalue $\omega_0, \omega_1, \cdots, \omega_{N-1}$. If (7) holds, it is trivially true that

$$\mathcal{H}^k P_N(\mathcal{H})\psi(q)\equiv 0, \qquad k=0, 1, \cdots, N-1 \tag{10}$$

for arbitrary $\psi(q)$. These $N$ simultaneous equations determine, in principle, the polynomial coefficients $a_0^{(N)}$, $a_1^{(N)}$, $\cdots$, $a_{N-1}^{(N)}$ and hence the $N$ eigenvalues.

For spectral distributions containing an infinite number of discrete eigenvalues or continuum regions, Eqs. (10) can no longer be identically satisfied for finite $N$. However, a polynomial $P_N(\omega)$ can always be found such that

$$\int dq\, f(q)\mathcal{H}^k P_N(\mathcal{H})\psi(q)=0, \qquad k=0, 1, \cdots, N-1, \tag{11}$$

where the additional arbitrary function $f(q)$ is restricted only by the condition that the integral exists. Once the set of polynomial coefficients $a_0^{(N)}, a_1^{(N)}, \cdots, a_{N-1}^{(N)}$ is determined, Eq. (9) can then be solved for $N$ *approximate* eigenvalues $\omega_0^{(N)}, \omega_1^{(N)}, \cdots, \omega_{N-1}^{(N)}$.

Three different computational approaches are given, depending on the choice of $f(q)$: the $\mu$ method (Sec. III), the $\nu$ method (Sec. VIII), and the $\lambda$ method (Sec. IX). Each is related to other quantum-mechanical approximation techniques.

## III. THE $\mu$ METHOD

For an arbitrary state function $\psi(q)$, energy moments are defined by[7]

$$\mu_k\equiv\int dq\,\psi^*(q)\mathcal{H}^k\psi(q). \tag{12}$$

If $\psi(q)$ is normalized,

$$\mu_0=\int dq\,\psi^*(q)\psi(q)=1. \tag{13}$$

When the Hamiltonian contains singularities, for example, those arising from Coulomb potentials, moments higher than some order (usually $k=2$) will generally diverge. Such cases (which include many problems of chemical interest) cannot be treated by the method developed in this section.

Assuming that moments of all orders do exist, let us choose $f(q)=\psi^*(q)$ in (11). Then

$$\int dq\psi^*(q)\mathcal{H}^k P_N(\mathcal{H})\psi(q)=0, \qquad k=0, 1, \cdots, N-1. \tag{14}$$

In terms of the energy moments (12), we can construct from (14) a set of $N$ simultaneous equations for the polynomial coefficients, viz.,

$$\begin{aligned}
&\mu_0 a_0^{(N)}+\mu_1 a_1^{(N)}+\cdots+\mu_{N-1}a_{N-1}^{(N)}=-\mu_N,\\
&\mu_1 a_0^{(N)}+\mu_2 a_1^{(N)}+\cdots+\mu_N a_{N-1}^{(N)}=-\mu_{N+1},\\
&\qquad\vdots\\
&\mu_{N-1}a_0^{(N)}+\mu_N a_1^{(N)}+\cdots+\mu_{2N-2}a_{N-1}^{(N)}=-\mu_{2N-1}.
\end{aligned} \tag{15}$$

The solutions of these inhomogeneous linear equations follow by Cramer's rule, whereby

$$a_k^{(N)}=D_k/D, \qquad k=0, 1, \cdots, N-1, \tag{16}$$

where

$$D=\begin{vmatrix} \mu_0 & \mu_1 & \cdots & \mu_{N-1}\\ \mu_1 & \mu_2 & \cdots & \mu_N\\ & & \cdot & \\ & & \cdot & \\ & & \cdot & \\ \mu_{N-1} & \mu_N & \cdots & \mu_{2N-2}\end{vmatrix} \tag{17}$$

and $D_k$ is formed from $D$ by replacing the $k$th column $[\mu_k\ \mu_{k+1}\cdots\mu_{k+N-1}]$ by $[\mu_N\ \mu_{N+1}\cdots\mu_{2N-1}]$. It is assumed that $D\neq 0$, which requires that there be at least $N$ distinct eigenvalues for the system described by $\mathcal{H}$ (see Sec. VII for proof). Once the coefficients $a_0^{(N)}, \cdots, a_{N-1}^{(N)}$ are known, (9) can be solved for the approximate ($N$th-order) eigenvalues. The foregoing procedure can be more compactly systematized as follows: Rearranging $D_k$ so that the last enumerated column appears on the left, we have

$$D_k=(-1)^{N+k+1}\times\begin{vmatrix} \mu_0 & \mu_1 & \cdots & \mu_{k-1} & \mu_{k+1} & \cdots & \mu_N\\ \mu_1 & \mu_2 & \cdots & \mu_k & \mu_{k+2} & \cdots & \mu_{N-1}\\ & & & \cdot & & & \\ & & & \cdot & & & \\ & & & \cdot & & & \\ \mu_{N-1} & \mu_N & \cdots & \mu_{k+N-1} & \mu_{k+N+1} & \cdots & \mu_{2N-1}\end{vmatrix}. \tag{18}$$

But this is just $(-1)^{N+1}$ times the $k$th term in the Laplace development for the $(N+1)\times(N+1)$ deter-

[7] Moments are denoted by $h_k$ in Refs. 5 and 6.

minant

$$\Delta_N(1)\equiv\begin{vmatrix} 1 & 1 & \cdots & 1 \\ \mu_0 & \mu_1 & \cdots & \mu_N \\ \mu_1 & \mu_2 & \cdots & \mu_{N+1} \\ & & \vdots & \\ \mu_{N-1} & \mu_N & \cdots & \mu_{2N-1} \end{vmatrix}. \tag{19}$$

Moreover,

$$\Delta_N(1)=(-1)^{N+1}[\sum_{k=0}^{N-1} D_k+D]. \tag{20}$$

But using (16),

$$\Delta_N(1)=(-1)^{N+1}D[\sum_{k=0}^{N-1} a_k{}^{(N)}+1]. \tag{21}$$

Defining the more general determinantal function,

$$\Delta_N(\omega)\equiv\begin{vmatrix} 1 & \omega & \cdots & \omega^N \\ \mu_0 & \mu_1 & \cdots & \mu_N \\ \mu_1 & \mu_2 & \cdots & \mu_{N+1} \\ & & \vdots & \\ \mu_{N-1} & \mu_N & \cdots & \mu_{2N-1} \end{vmatrix}. \tag{22}$$

We have analogously

$$\Delta_N(\omega)=(-1)^{N+1}D[\sum_{k=0}^{N-1} a_k{}^{(N)}\omega^k+\omega^N]. \tag{23}$$

But the bracketed quantity can be identified as the polynomial $P_N(\omega)$, [cf. Eq. (9)]. Therefore the $N$ approximate eigenvalues in an $N$th-order calculation appear as the roots of the determinantal equation

$$\Delta_N(\omega)=0. \tag{24}$$

It can be shown that the $N$ roots of (24) are real and distinct. Also, the polynomials $\Delta_N(\omega)$ comprise an orthogonal set with respect to the weighting function $G(\omega)$, the spectral function [cf. Eq. (5)], i.e.,

$$\int d\omega\, G(\omega)\Delta_N(\omega)\Delta_{N'}(\omega)=0, \qquad N\neq N'. \tag{25}$$

The entire formalism can, in fact, be based on the properties of orthogonal polynomials and their associated distributions.[8]

The approximate eigenfunctions $\phi_0{}^{(N)}(q)$, $\phi_1{}^{(N)}(q)$, $\cdots$, $\phi_{N-1}{}^{(N)}(q)$ corresponding to the $N$th-order eigenvalues $\omega_0{}^{(N)}$, $\omega_1{}^{(N)}$, $\cdots$, $\omega_{N-1}{}^{(N)}$ can be generated by projection operators, i.e.,

$$\phi_n{}^{(N)}(q)=\frac{P_N(\mathcal{H})}{\mathcal{H}-\omega_n}\psi(q)\equiv\prod_{m=0,(m\neq n)}^{N-1}(\mathcal{H}-\omega_m{}^{(N)})\psi(q). \tag{26}$$

This is shown as follows:

$$\int dq\,\phi_n{}^{(N)*}(q)\,(\mathcal{H}-\omega_n{}^{(N)})\phi_n{}^{(N)}(q)$$

$$=\int dq\,\phi_n{}^{(N)*}(q)\,P_N(\mathcal{H})\psi(q)$$

$$=\int dq\,\psi^*(q)\prod_{m\neq n}(\mathcal{H}-\omega_m{}^{(N)})\,P_N(\mathcal{H})\psi(q)=0. \tag{27}$$

The first equality follows from (6). Recognizing that the projection operator is an $(N-1)$ degree polynomial in $\mathcal{H}$, the last equality results from successive application of (14). The vanishing of the first integral in (27) identifies $\phi_n{}^{(N)}(q)$ as the eigenfunction corresponding to $\omega_n{}^{(N)}$.

## IV. CONNECTION WITH THE METHOD OF MOMENTS

Any function $\psi(q)$ obeying the limitations we have set forth can formally be expanded in terms of the eigenfunctions of $\mathcal{H}$:

$$\psi(q)=\mathbf{S}_n\, c_n\phi_n(q), \tag{28}$$

where the generalized summation symbol $\mathbf{S}_n$ combines summation over the discrete states with integration over the continuum. In terms of (28), the moments (12) can be expressed

$$\mu_k=\mathbf{S}_n\,|\,c_n\,|^2\omega_n{}^k. \tag{29}$$

The function $|\,\psi(q)\,|^2$, as well as the eigenvalue spectrum $G(\omega)$, have obvious analogies with probability distributions. Certain results in probability theory pertaining to continuous distributions, in particular, the method of moments, should therefore be applicable to these quantum-mechanical analogs. For example, the moments, if all exist, uniquely determine a distribution, provided that the sum

$$\sum_{k=0}^{\infty}\mu_k{}^{-1/2k}$$

is divergent (Carleman's theorem).[9] For every distribution (including the eigenvalue spectrum) there can be found a corresponding discrete distribution for which the first $2N$ moments coincide. For example, if, for a

[8] See, for example, G. Szegö, *Orthogonal Polynomials* (American Mathematical Society Colloquim Publications, New York, 1939), Vol. 23.

[9] T. Carleman, *Les Fonctions Quasi Analytique* (Gauthier Villars, Paris, 1926), p. 80. The theorem was applied to the phonon–polaron problem by F. R. Halpern, Phys. Rev. 111, 1 (1958).

state function $\psi(q)$, $2N$ moments $\mu_0, \mu_1, \cdots, \mu_{2N-1}$ are evaluated using (12), there exists an equivalent distribution characterized by the discrete eigenvalues $\omega_0^{(N)}$, $\omega_1^{(N)}, \cdots, \omega_{N-1}^{(N)}$ for which

$$\mu_k=\sum_{n=0}^{N-1} b_n^{(N)}[\omega_n^{(N)}]^k, \qquad k=0, 1, \cdots, 2N-1. \quad (30)$$

These $2N$ simultaneous equations suffice, in principle, to determine $N$ approximate eigenvalues $\omega_n^{(N)}$ together with $N$ distribution coefficients $b_n^{(N)}$. Let the $\omega_k^{(N)}$'s be the roots of a polynomial $P_N(\omega)$ such as (9). Then we have, as well,

$$\omega^k P_N(\omega)=0, \qquad k=0, 1, \cdots, N-1. \quad (31)$$

Insert $\omega_0^{(N)}, \omega_1^{(N)}, \cdots, \omega_{N-1}^{(N)}$ successively into the first of (31), multiply respectively by $b_0^{(N)}, b_1^{(N)}, \cdots, b_{N-1}^{(N)}$, and sum the $N$ equations so obtained. The result is, by virtue of (30),

$$a_0^{(N)}\mu_0+a_1^{(N)}\mu_1+\cdots+a_{N-1}^{(N)}\mu_{N-1}+\mu_N=0. \quad (32)$$

Repeating the procedure on successive members of (31), we obtain a set of equations identical to (15). This demonstrates the equivalence of the two approaches. There exists a unique solution to (30) if, and only if, the exact expansion (29) contains (in the absence of continuum contributions) at least $N$ terms. It should also be noted that a set of degenerate states accounts for but a single eigenvalue and, conversely, that the method does not determine the degeneracy of any state.

## V. CONNECTION WITH THE VARIATIONAL PRINCIPLE

For a set of $N$ basis functions

$$\chi_k(q)=\mathcal{H}^k\psi(q), \qquad k=0, 1, \cdots, N-1, \quad (33)$$

let the optimal linear combination

$$\Psi(q)=(\sum_{k=0}^{N-1} c_k^{(N)}\mathcal{H}^k)\psi(q)=\sum_{k=0}^{N-1} c_k^{(N)}\chi_k(q) \quad (34)$$

be determined in accordance with the variational principle

$$\delta\omega=0 \quad (35)$$

where

$$\omega=\left[\int dq\, \Psi^*(q)\mathcal{H}\Psi(q) \Big/ \int dq\, |\Psi(q)|^2\right]. \quad (36)$$

Variational functions of the type

$$\Psi(q)=(c_0+c_1V)\psi(q) \quad (37)$$

were employed by Hassé[10] in calculations of atomic polarizabilities. These represent, in our nomenclature, second-order calculations since moments up to $\mu_3$ are contained in the energy expectation value.

The requisite matrix elements $H_{mn}$ and $S_{mn}$ are related to the moments (12) as follows:

$$H_{mn}=\int dq\, \chi_m^*(q)\mathcal{H}\chi_n(q)=\mu_{m+n+1} \quad (38)$$

and

$$S_{mn}=\int dq\, \chi_m^*(q)\chi_n(q)=\mu_{m+n} \quad (39)$$

by virtue of (33) and the Hermitian property of $\mathcal{H}$.

The secular equation

$$\det|H_{mn}-\omega S_{mn}|=0 \quad (40)$$

thereby takes the form

$$\begin{vmatrix} \mu_1-\omega\mu_0 & \mu_2-\omega\mu_1 & \cdots & \mu_N-\omega\mu_{N-1} \\ \mu_2-\omega\mu_1 & \mu_3-\omega\mu_2 & \cdots & \mu_{N+1}-\omega\mu_N \\ & \vdots & & \\ \mu_N-\omega\mu_{N-1} & \mu_{N+1}-\omega\mu_N & \cdots & \mu_{2N-1}-\omega\mu_{2N-2} \end{vmatrix}=0. \quad (41)$$

That this is equivalent to Eq. (24) is shown as follows: From the second column of $\Delta_N^{(\omega)}$ [Eq. (22)] subtract $\omega$ times the first column. The determinant is, of course, invariant under such an operation. From the third column subtract $\omega$ times the second column, and so on. The result is

$$\Delta_N(\omega)=\begin{vmatrix} 1 & 0 & 0 & \cdots & 0 \\ \mu_0 & \mu_1-\omega\mu_0 & \mu_2-\omega\mu_1 & \cdots & \mu_N-\omega\mu_{N-1} \\ \mu_1 & \mu_2-\omega\mu_1 & \mu_3-\omega\mu_2 & \cdots & \mu_{N+1}-\omega\mu_N \\ & & \vdots & & \\ \mu_N & \mu_{N+1}-\omega\mu_N & \mu_{N+2}-\omega\mu_{N+1} & \cdots & \mu_{2N-1}-\omega\mu_{2N-2} \end{vmatrix}. \quad (42)$$

[10] E. R. Hassé, Proc. Cambridge Phil. Soc. **26**, 542 (1930); J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

Finally, a Laplace development about the top row leads to (41). Therefore, the $\mu$ method and the method of moments are both equivalent to a linear variational treatment on the basis (33). From this follow the well-known variational results that the approximate eigenvalues are real and distinct and that they interleave with the exact eigenvalues.[11] In particular, the lowest calculated eigenvalue provides an upper bound for the ground state

$$\omega_0^{(N)} \geq \omega_0. \tag{43}$$

The approximate eigenfunctions determined by solving for the coefficients $c_k^{(N)}$ correspond to those given by (26).

## VI. CONNECTION WITH EIGENVALUE SPECTROSCOPY

Suppose that for some $\psi(q)$, the first $2N$ moments have been evaluated explicitly. In accordance with Sec. IV, these can be expressed in terms of an equivalent distribution using (30), i.e.,

$$\mu_k = \sum_{n=0}^{N-1} b_n^{(N)} [\omega_n^{(N)}]^k, \qquad k=0, 1, \cdots, 2N-1. \tag{44}$$

The approximation is now made that (44) *also* applies to the higher moments, i.e.,

$$\mu_k \approx \sum_{n=0}^{N-1} b_n^{(N)} [\omega_n^{(N)}]^k, \qquad k=2N, 2N+1, \cdots, \infty \tag{45}$$

with the same $b_n^{(N)}$ and $\omega_n^{(N)}$ as determined from the $N$th-order calculation. Substituting (44) and (45) into (5), we obtain

$$G(\omega) \approx 2\pi \sum_{k=0}^{\infty} \sum_{n=0}^{N-1} b_n^{(N)} \frac{(-1)^k}{k!} [\omega_n^{(N)}]^k \delta^{(k)}(\omega). \tag{46}$$

For each $n$, the summation over $k$ represents a formal Taylor series expansion for $\delta(\omega - \omega_n^{(N)})$. Therefore,

$$G(\omega) \approx 2\pi \sum_{n=0}^{N-1} b_n^{(N)} \delta(\omega - \omega_n^{(N)}), \tag{47}$$

showing that the $N$ approximate eigenvalues, each of which shows up as a delta function, are identical to those determined by the method of moments. Evidently, as $N$ is increased, so that more of the moments are given exactly, (47) approaches the actual eigenvalue spectrum.

## VII. EXISTENCE OF SOLUTIONS; CONVERGENCE

Let us first suppose that the expansion (28) or (29) contains only a finite number, say $M$, of discrete eigenstates or, equivalently, that only $M$ functions of the basis (33) are linearly independent. In this instance (29) becomes

$$\mu_k = \sum_{n=0}^{M-1} |c_n|^2 \omega_n^k. \tag{48}$$

Substituting the expansions (48) for each element of the determinant $D$ [Eq. (17)] and applying, successively, the determinantal identity

$$\begin{vmatrix} \vdots & & & \\ \sum_{\alpha=0}^{M-1} A_{\alpha 0} & \sum_{\alpha=0}^{M-1} A_{\alpha 1} & \cdots & \sum_{\alpha=0}^{M-1} A_{\alpha N} \\ \vdots & & & \end{vmatrix} = \sum_{\alpha=0}^{M-1} \begin{vmatrix} \vdots & & & \\ A_{\alpha 0} & A_{\alpha 1} & \cdots & A_{\alpha N} \\ \vdots & & & \end{vmatrix}, \tag{49}$$

we obtain

$$D = \sum_{\alpha=0}^{M-1} \sum_{\beta=0}^{M-1} \cdots \sum_{\nu=0}^{M-1} |c_\alpha|^2 |c_\beta|^2 \cdots |c_\nu|^2 \times \begin{vmatrix} 1 & \omega_\alpha & \omega_\alpha^2 & \cdots & \omega_\alpha^{N-1} \\ \omega_\beta & \omega_\beta^2 & \omega_\beta^3 & \cdots & \omega_\beta^N \\ & & \vdots & & \\ \omega_\nu^{N-1} & \omega_\nu^N & \omega_\nu^{N+1} & \cdots & \omega_\nu^{2N-2} \end{vmatrix}. \tag{50}$$

Now any determinant in (50) will vanish whenever any two indices $\alpha, \beta, \cdots, \nu$ coincide, for then two rows will be proportional. However, two indices will be forced into equality whenever $N > M$. Therefore $D$, and correspondingly $\Delta_N(\omega)$, of which $D$ is a minor, will vanish identically if $N > M$. In this instance a unique solution will not exist for the $\mu$ method as formulated in Secs. III–V. This difficulty does not, however, arise in eigenvalue spectroscopy (Sec. VI). The $\mu$ method can be made operative by removing the redundant moments $\mu_{2M}, \mu_{2M+1}, \cdots$ by using the largest nonvanishing minor in $D$. To summarize, Eqs. (24), (30), or (41) possess unique solutions provided that $M \geq N$ and that at least $2N$ moments $(\mu_0, \cdots, \mu_{2N-1})$ exist. These alternative sets of $2N$ simultaneous equations then suffice to determine $N$ approximate eigenvalues (exact if $M=N$) and $N$ expansion coefficients for the arbitrary state function $\psi(q)$. From the latter set, or using (26), the approximate eigenfunctions can be constructed.

[11] J. K. L. MacDonald, Phys. Rev. **43**, 830 (1933).

As to the convergence of the calculated eigenvalues and eigenfunction to exact ones, the following conjecture is made: If it is found that linear dependence is approached as $N\to\infty$ as indicated, for example, by $\Delta_N(\omega)$ approaching zero identically, the calculated eigenvalues and eigenfunctions are converging to exact ones. This generalization is based on intuition and experience; we have not pursued it on a rigorous level, particularly in cases involving continuous spectra.

Analogous considerations apply to existence and convergence for the $\nu$ and $\lambda$ methods.

## VIII. THE $\nu$ METHOD

One way of circumventing the moment-divergence difficulty might be to modify the potentials. Replacing $r^{-1}$ by $(r+b)^{-1}$ in Coulomb potentials for example, removes the singularity. The $\mu$ method is then applicable, with $b$ carried as a parameter. It can be shown that, although individual moments may diverge as $b\to 0$, they do so in a compensating manner such that the approximate eigenvalues approach finite limits. An alternative approach might be to transform the Hamiltonian so as to remove the singularities. The two-particle Coulombic system can, for example, be transformed into the harmonic oscillator.[12] Analogous transformations might well be possible for many-particle systems.

The method to be outlined in this section avoids not only the divergence problem but the evaluation of integrals entirely. The $\nu$ method is based on the choice $f(q)=\delta(q-q')$ in (11), where $q'$ represents an arbitrary point in the configuration space sufficiently distant from any singularity. Defining the semimoments[13]

$$\nu_k(q')\equiv\int dq\,\delta(q-q')\mathcal{H}^k\psi(q)=[\mathcal{H}^k\psi(q)]_{q=q'}=\chi_k(q'), \tag{51}$$

we can construct a set of equations analogous to (15) but with $\nu_k(q')$ instead of $\mu_k$. Subsequent developments are, *mutatis mutandis*, largely analogous. Thus, an $N$th-order calculation, requiring $2N$ semimoments, leads to approximations for $N$ eigenvalues (depending on $q'$ and different, in general, from those obtained by the corresponding moment calculation). The computational accessibility of the semimoments is the principal advantage of the $\nu$ method. For the most common types of Hamiltonian operators, evaluation of $\nu_k(q')$ involves only the operations of differentiation and multiplication.

The $\nu$ method also has a variational analog. Consider the trial function

$$\Phi(q)=\Big(\sum_{k=0}^{N-1}c_k^{(N)}\mathcal{H}^k\Big)^\dagger\Big(\sum_{k=0}^{N-1}c_k^{(N)}\mathcal{H}^k\Big)\psi(q)$$

$$=\sum_{k=0}^{N-1}\sum_{m=0}^{N-1}c_k^{(N)*}c_m^{(N)}\chi_{k+m}(q), \tag{52}$$

where (33) has been used for the last equality. Specify now that the local energy[14]

$$\omega^{(N)}(q)\equiv\mathcal{H}\Phi(q)/\Phi(q) \tag{53}$$

shall be stationary with respect to variations in the $C_k^{(N)}$, i.e.,

$$\delta\omega^{(N)}(q)=\{\delta[\mathcal{H}\Phi(q)]/\Phi(q)\}$$
$$-\{[\mathcal{H}\Phi(q)]\delta\Phi(q)/[\Phi(q)]^2\}=0; \tag{54}$$

multiplying by $\Phi(q)$ and using (53) again, the variational condition can be written

$$\delta[\mathcal{H}\Phi(q)-\omega^{(N)}(q)\Phi(q)]=0; \tag{55}$$

substituting the expansion (52), noting that $\mathcal{H}\chi_{k+m}=\chi_{k+m+1}$, and setting $q=q'$, which introduces the semimoments [cf. (51)], we obtain

$$\delta\sum_k\sum_m c_k^{(N)*}c_m^{(N)}[\nu_{k+m+1}(q')-\omega^{(N)}(q')\nu_{k+m}(q')]=0. \tag{56}$$

In analogy with the conventional variational problem (Sec. V), this leads to a secular equation

$$\begin{vmatrix} \nu_1(q')-\omega\nu_0(q') & \nu_2(q')-\omega\nu_1(q') & \cdots & \nu_N(q')-\omega\nu_{N-1}(q') \\ \nu_2(q')-\omega\nu_1(q') & \nu_3(q')-\omega\nu_2(q') & \cdots & \nu_{N+1}(q')-\omega\nu_N(q') \\ & \vdots & & \\ \nu_N(q')-\omega\nu_{N-1}(q') & \nu_{N+1}(q')-\omega\nu_N(q') & \cdots & \nu_{2N-1}(q')-\omega\nu_{2N-2}(q') \end{vmatrix}=0, \tag{57}$$

where the $N$ roots represent extremal values of the local energy $\omega^{(N)}(q')$.

[12] D. Bergmann and Y. Frishman, J. Math. Phys. 6, 1855 (1965).
[13] Semimoments are denoted by $h_k(q')$ in Refs. 5 and 6.
[14] J. H. Bartlett, Phys. Rev. 51, 661 (1937).

TABLE I. Coefficients $A_n^{(k)}$.

| | k | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| n | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 0 | 1 | | | | | | | |
| 1 | 1 | −1.5 | | | | | | |
| 2 | 2.5 | −9 | 2.25 | | | | | |
| 3 | 11.5 | −62.25 | 33.75 | −3.375 | | | | |
| 4 | 73.75 | −531.0 | 447.75 | −9.45 | 5.06 | | | |
| 5 | $6.048\times10^{2}$ | $-5.452\times10^{3}$ | $6.243\times10^{3}$ | $-2.041\times10^{3}$ | $2.278\times10^{2}$ | −7.593 | | |
| 6 | $6.056\times10^{3}$ | $-6.563\times10^{4}$ | $9.500\times10^{4}$ | $-42.29\times10^{4}$ | $7.277\times10^{3}$ | $-5.012\times10^{2}$ | 11.39 | |
| 7 | $7.169\times10^{4}$ | $-9.072\times10^{5}$ | $1.588\times10^{6}$ | $-8.960\times10^{5}$ | $2.097\times10^{5}$ | $2.219\times10^{4}$ | $1.036\times10^{3}$ | −17.08 |

In analogy with (24), the latter can also be obtained from the determinantal equation

$$\begin{vmatrix} 1 & \omega & \cdots & \omega^N \\ \nu_0(q') & \nu_1(q') & \cdots & \nu_N(q') \\ \nu_1(q') & \nu_2(q') & \cdots & \nu_{N+1}(q') \\ & & \vdots & \\ \nu_{N-1}(q') & \nu_N(q') & \cdots & \nu_{2N-1}(q') \end{vmatrix} = 0. \quad (58)$$

The variational condition (54) implies only stationarity, in contrast to (35), which also implies minimization. The roots of (57) or (58) are therefore *not* upper bounds on the corresponding exact eigenvalues. In common with local energy method, fluctuations in the $\omega(q')$ with $q'$ should decrease with improvement of the trial function $\Phi(q)$, hence with higher-order $N$.

## IX. THE λ METHOD

$N$ conditions on the polynomial coefficients $a_0^{(N)}, \cdots, a_{N-1}^{(N)}$ can also be imposed by choosing in (11), with $k=0$, $f(q)$ successively equal to $\delta(q-q_m)$, for $N$ distinct points $q_0, q_1, \cdots q_{N-1}$ in configuration space. In terms of the quantities

$$\lambda_{km} \equiv [\mathcal{H}^k\psi(q)]_{q=q_m} = \nu_k(q_m), \quad (59)$$

we obtain the $N$ simultaneous equations

$$\begin{aligned} &\lambda_{00}a_0^{(N)}+\lambda_{10}a_1^{(N)}+\cdots+\lambda_{N-1,0}a_{N-1}^{(N)} = -\lambda_{N0}, \\ &\lambda_{01}a_0^{(N)}+\lambda_{11}a_1^{(N)}+\cdots+\lambda_{N-1,1}a_{N-1}^{(N)} = -\lambda_{N1}, \\ &\qquad\vdots \\ &\lambda_{0,N-1}a_0^{(N)}+\lambda_{1,N-1}a_1^{(N)}+\cdots+\lambda_{N-1,N-1}a_{N-1}^{(N)} \\ &\qquad = -\lambda_{N,N-1}. \end{aligned} \quad (60)$$

Exploiting the analogy between (60) and (15), the λ method leads to $N$ approximate eigenvalues which are the roots of the determinantal equation

$$\begin{vmatrix} 1 & \omega & \cdots & \omega^N \\ \lambda_{00} & \lambda_{10} & \cdots & \lambda_{N0} \\ \lambda_{01} & \lambda_{11} & \cdots & \lambda_{N1} \\ & & \vdots & \\ \lambda_{0,N-1} & \lambda_{1,N-1} & \cdots & \lambda_{N,N-1} \end{vmatrix} = 0. \quad (61)$$

The approximate eigenvalues represent averages of local energies (53) over the configuration points $q_0$, $q_1$, $\cdots$, $q_{N-1}$. Weighting factors on these points can be introduced, if desired. Although the λ matrix is not symmetrical ($\lambda_{km}\neq\lambda_{mk}$), this method has the computational advantage over the $\mu$ and $\nu$ methods that only moments up to order $N$ (rather than $2N-1$) need be computed. The λ method has certain features in common with Frost's least-squares local-energy method.[15] If the latter were, in fact, carried out using the basis (33) and the configuration points $q_0, \cdots, q_{N-1}$, then the two methods would become very nearly equivalent.

## X. A THEOREM ON LOWER BOUNDS

More information about the over-all distribution of eigenvalues is contained in $N$ moments than in any other set of $N$ parameters, except, perhaps, $N$ of the eigenvalues themselves. This is one advantage of the method of moments over other quantum-mechanical computational methods. For example, several criteria on lower bounds to the lowest eigenvalue make use of energy moments. Weinstein's criterion,[16] in particular, requires the second moment. We shall derive here a generalization of Weinstein's criterion based on quantities which are determined in the course of a moments calculation.

[15] A. A. Frost, J. Chem. Phys. **10**, 240 (1942); A. A. Frost, R. E. Kellogg, and E. C. Curtis, Rev. Mod. Phys. **32**, 313 (1960); and subsequent publications of Frost and co-workers.

[16] D. H. Weinstein, Proc. Nat. Acad. Sci. U.S. **20**, 529 (1934); L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., New York, 1935), p. 189.

TABLE II. Approximate eigenvalues $\omega_n^{(N)}$ and expansion coefficients $b_n^{(N)}$.

| | $n$ | | | | | |
|---|---|---|---|---|---|---|
| $N$ | 0 | 1 | 2 | 3 | 4 | 5 |
| 1 | 0.625<br>1.00 | | | | | |
| 2 | 0.51715<br>0.96029 | 3.2328<br>$3.971\times10^{-2}$ | | | | |
| 3 | 0.50235<br>0.94614 | 2.6890<br>$5.243\times10^{-2}$ | 6.1857<br>$1.426\times10^{-3}$ | | | |
| 4 | 0.50030<br>0.94333 | 2.5452<br>$5.329\times10^{-2}$ | 5.1063<br>$3.328\times10^{-3}$ | 9.3472<br>$4.230\times10^{-5}$ | | |
| 5 | 0.50003<br>0.94288 | 2.5097<br>$5.273\times10^{-2}$ | 4.7119<br>$4.208\times10^{-3}$ | 7.7644<br>$1.761\times10^{-4}$ | 12.649<br>$1.123\times10^{-6}$ | |
| 6 | 0.50002<br>0.94279 | 2.5060<br>$5.230\times10^{-2}$ | 4.6522<br>$4.463\times10^{-3}$ | 7.5016<br>$4.310\times10^{-4}$ | 11.9019<br>$1.470\times10^{-5}$ | 21.855<br>$5.320\times10^{-8}$ |
| 7 | 0.50000<br>0.94277 | 2.5008<br>$5.215\times10^{-2}$ | 4.5464<br>$4.478\times10^{-3}$ | 6.9776<br>$5.732\times10^{-4}$ | 10.465<br>$2.257\times10^{-5}$ | 15.901<br>$8.723\times10^{-8}$ |
| 8 | 0.50000<br>0.94277 | 2.4998<br>$5.212\times10^{-2}$ | 4.5185<br>$4.478\times10^{-3}$ | 6.8404<br>$6.063\times10^{-4}$ | 10.177<br>$2.413\times10^{-5}$ | 15.413<br>$9.341\times10^{-8}$ |

The variance $\sigma^2$ of a distribution is defined by

$$\sigma^2=\mu_2-\mu_1^2. \tag{62}$$

In terms of the formal expansions (29) and assuming normalization,

$$\sigma^2=\sum_n |c_n|^2\omega_n^2-\left(\sum_n |c_n|^2\omega_n\right)^2=\tfrac{1}{2}\sum_{n\,m}\sum |c_m|^2|c_n|^2(\omega_n-\omega_m)^2$$
$$=\sum_{n\geq m}\sum |c_n|^2|c_m|^2(\omega_n-\omega_m)^2. \tag{63}$$

Since each term in the double summation is positive definite,

$$\sigma^2\geq\sum_n |c_n|^2|c_0|^2(\omega_n-\omega_0)^2=|c_0|^2(\mu_2-2\omega_0\mu_1+\omega_0^2)$$
$$=|c_0|^2[\sigma^2+(\mu_1-\omega_0)^2]. \tag{64}$$

In accordance with the variational principle $\mu_1\geq\omega_0$; solving (64) for $\omega_0$ therefore leads to a complementary inequality

$$\omega_0\geq\mu_1-(|c_0|^{-2}-1)^{1/2}\sigma. \tag{65}$$

Thus, if $|c_0|^2$ or a lower bound on $|c_0|^2$ is known, (65) provides a lower bound to the ground-state eigenvalue.

For the case $|c_0|^2=\frac{1}{2}$, (65) reduces to Weinstein's criterion

$$\omega_0\geq\mu_1-\sigma; \tag{66}$$

when $|c_0|^2>\frac{1}{2}$, (65) provides a sharper condition on the lower bound.

## XI. APPLICATION TO THE HARMONIC OSCILLATOR

The quantum-mechanical method of moments will be applied to the linear harmonic oscillator. For unit mass and force constant, the system is described by the Hamiltonian

$$\mathcal{H}=-\tfrac{1}{2}(d^2/dx^2)+\tfrac{1}{2}x^2. \tag{67}$$

The exact solutions to the Schrödinger equation are, of course, well known for this problem:

$$\omega_n=n+\tfrac{1}{2},$$
$$\phi_n(x)=(2^n n!\pi^{1/2})^{-1/2}H_n(x)\exp(-x^2/2),$$
$$n=0,\,1,\,2\cdots, \tag{68}$$

where $H_n(x)$ are the Hermite polynomials.

As the approximation function, we choose the non-eigenfunction

$$\psi(x)=\pi^{-1/4}\exp(-x^2). \tag{69}$$

This is expandable in the even-parity eigenfunctions (68). The approximate eigenvalues should then approach the set $\frac{1}{2}, 2\frac{1}{2}, 4\frac{1}{2}, \cdots$.

The computation of moments is considerably simplified by the fact that operation of (67) on (69) brings down even powers of $x$ multiplying $\psi(x)$. We can therefore write

$$\mathcal{H}^k\psi(x)=\mathfrak{A}_k(x)\psi(x), \tag{70}$$

where $\mathfrak{A}_k(x)$ is a polynomial

$$\mathfrak{A}_k(x)=\sum_n A_n^{(k)}x^{2n} \tag{71}$$

with $\mathfrak{A}_0(x)=1$. If $\mathfrak{A}_k(x)$ is known, the next higher polynomial can be obtained from

$$\mathfrak{A}_{k+1}(x)\psi(x)=\mathcal{H}\mathfrak{A}_k(x)\psi(x)=\sum_m A_m^{(k)}\mathcal{H}x^{2m}\psi(x). \tag{72}$$

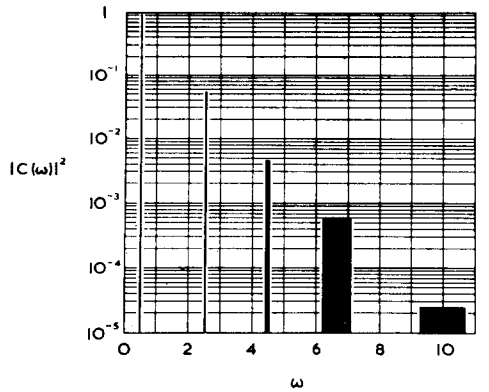


FIG. 1. Calculated eigenvalue spectrum for harmonic oscillator.

Define the new polynomial

$$\mathcal{B}_m(x) = \sum_r B_{mr} x^r \tag{73}$$

such that

$$\mathcal{H} x^{2m} \exp(-x^2) = \mathcal{B}_m(x) \exp(-x^2). \tag{74}$$

Then

$$\mathcal{A}_{k+1}\psi(x) = \sum_m A_m^{(k)} \sum_r B_{mr} x^{2r} \psi(x), \tag{75}$$

the coefficient of $x^{2r}$ in $\mathcal{A}_{k+1}$ being

$$A_r^{(k+1)} = \sum_m A_m^{(k)} B_{mr}. \tag{76}$$

This can be expressed in matrix form as

$$\mathbf{A}^{(k+1)} = \mathbf{A}^{(k)}\mathbf{B}, \tag{77}$$

where $\mathbf{A}^{(k)}$ is the row vector with elements $A_n^{(k)}$. For this problem, it is easily shown that the matrix $\mathbf{B}$ is tridiagonal with

$$\begin{aligned} B_{nn} &= 2n+1, \\ B_{n,n+1} &= -3/2, \\ B_{n,n-1} &= -n(n-1)/2, \end{aligned} \tag{78}$$

all other elements vanishing.

The moments, semimoments, and $\lambda$ coefficients now follow in straightforward fashion. In terms of

$$\begin{aligned} C_n &= \int_{-\infty}^{\infty} x^{2n} \exp(-2x^2)\, dx, \\ C_n' &= x'^{2n} \exp(-x'^2), \\ C_{nm}'' &= x_m^{2n} \exp(-x_n^2), \end{aligned} \tag{79}$$

we obtain, in matrix notation,

$$\begin{aligned} \mu_k &= \mathbf{A}^{(k)}\mathbf{C}, \\ \nu_k(x') &= \mathbf{A}^{(k)}\mathbf{C}', \\ \lambda_{km} &= \mathbf{A}^k\mathbf{C}''^{(m)}, \end{aligned} \tag{80}$$

where the $\mathbf{C}$'s are the appropriate column vectors with elements given by (79). The procedure outlined here is suitable for computer programming. It can be applied to calculate moments of almost arbitrarily high order. The method can also be generalized for many-dimensional problems.

The method of moments has been carried to eighth order on the IBM 7090 computer. The vectors $\mathbf{A}^{(0)}, \cdots, \mathbf{A}^{(7)}$ are tabulated in Table I. The general pattern is clear from these, so higher-order vectors are not enumerated. For the larger values of $k$, it is seen that $A_k^{(k)}$ is much smaller in magnitude than the other elements of $\mathbf{A}^{(k)}$. If $A_{2N-1}^{(2N-1)}$ were exactly zero, $\mathbf{A}^{(2N-1)}$ would be expressible as a linear combination of the $\mathbf{A}^{(k)}$ with $k<2N-1$. The basis set $\chi_0, \cdots, \chi_{2N-1}$ would thereby be linearly dependent, and the $N$th-order calculation would give $N$ exact eigenvalues and eigenfunctions. The fact that $A_k^{(k)}$ becomes less and less significant on a relative scale indicates that the basis is approaching linear dependence as $N\to\infty$ and, thus, that the approximate eigenvalues and eigenfunctions are converging to exact ones.

Table II gives the six lowest eigenvalues $\omega_n^{(N)}$ and expansion coefficients $b_n^{(N)}$ for moment calculations up to eighth order. These are the best results based on two independent calculations. By choosing different normalization constants, round-off and other machine errors could be varied. These errors produced up to 5% variation in the higher eigenvalues for the eighth-order calculation. Since these calculations are mainly exploratory in nature, no further attempts were made to improve computational precision. The best results are represented graphically in Fig. 1. The widths of the eigenvalue peaks correspond roughly to the computational errors.

To apply the lower-bound criterion (65), $|c_0|^2$ can be identified with $b_0^{(N)}$ obtained from the eighth-order calculation. The expansion coefficient has apparently converged to the value 0.94277. With $\mu_1=0.625$, $\sigma=0.53033$, we obtain $\omega_0\geq 0.4944$. This is, in any case, a considerable improvement over Weinstein's criterion, which gives $\omega_0\geq 0.0946$.

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