Energy Calculation by the Method of Local Moments*

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(Received 25 July 1967)

A new method for obtaining energies without integrals, which combines the formalism of the "method of moments" with the spirit of the "local-energy method," is proposed. This "method of local moments" avoids some of the convergence difficulties of the method of moments and some of the arbitrariness of the local-energy method. Advantages and disadvantages are discussed, and some features of the method are illustrated by examples. Several generalized versions of the method are also discussed.

I. INTRODUCTION

Evaluation of integrals is a major difficulty in quantum-chemical energy calculations. One approach to avoiding integrals is the "local-energy" method (LEM) of Frost.[1] (It is possible, however, to regard the LEM as a particular approach to numerical integration.[1]) We propose here a new method for obtaining energies without integrals. Because this method is suggested by the conventional method of moments[2] (MM) and has some of the spirit of the LEM, we call it the "method of local moments" (MLM). In particular, the secular equation for the energy is identical in form to the basic equation of the MM [see Eq. (11) below], but the conventional moments of the Hamiltonian $\langle\phi, H^k\phi\rangle/\langle\phi, \phi\rangle$ are replaced by local versions $H^k\phi(\mathbf{x}_0)/\phi(\mathbf{x}_0)$. Since no integrals are needed, basis functions with complicated r_{ij} dependence can be used for many-electron problems. Furthermore, some of the arbitrariness of the LEM and some of the convergence difficulties of the MM are avoided.

II. LOCAL-MOMENT LEMMA

Our method for calculating energies is based on the following lemma:

Lemma: Let H be any Hamiltonian, and let ψ be a function which can be expressed as a linear combination of the eigenfunctions of H. If at the point $\mathbf{x}=\mathbf{x}_0$ of the configuration space of H,

$$\psi(\mathbf{x}_0)\neq 0, \tag{1}$$

and if

$$H^k\psi(\mathbf{x}_0)=E^k\psi(\mathbf{x}_0), \qquad (k=1, 2, \cdots, \infty), \tag{2}$$

then E is an eigenvalue of H.

To prove the lemma, first expand ψ on the eigenfunctions χ_i of H:

$$H\chi_i(\mathbf{x})=E_i\chi_i(\mathbf{x}), \tag{3}$$

$$\psi(\mathbf{x})=\sum_{i=1}^{\infty}c_i\chi_i(\mathbf{x}). \tag{4}$$

(For simplicity, we have taken the spectrum of H to be discrete.) Next compute $\exp[-\lambda(E-H)^2]\psi(\mathbf{x}_0)$, where λ is an arbitrary parameter. From Eq. (2), one obtains

$$\exp[-\lambda(E-H)^2]\psi(\mathbf{x}_0)=\psi(\mathbf{x}_0). \tag{5}$$

From Eqs. (3)–(5), $\psi(\mathbf{x}_0)$ is given by

$$\psi(\mathbf{x}_0)=\sum_{i=1}^{\infty}\exp[-\lambda(E-E_i)^2]c_i\chi_i(\mathbf{x}_0). \tag{6}$$

The left-hand side of Eq. (6) is independent of λ and $\neq 0$ [Eq. (1)]. We evaluate the right-hand side at a convenient value of λ, $\lambda=\infty$. When $E_i\neq E$, $\exp[-\lambda(E-E_i)^2]\to 0$ as $\lambda\to\infty$. Thus all the terms in Eq. (6) for which $E_i\neq E$ contribute zero. Since the sum is finite and $\neq 0$, the E must coincide with some eigenvalue of H, say E_j, and then

$$E=E_j, \tag{7}$$

$$\psi(\mathbf{x}_0)=\exp[-\lambda(E-E_j)^2]c_j\chi_j(\mathbf{x}_0) \tag{8}$$

$$=c_j\chi_j(\mathbf{x}_0) \tag{9}$$

$$\neq 0. \tag{10}$$

Q.E.D.

* Supported in part by a National Science Foundation Grant.

[1] (a) A. A. Frost, J. Chem. Phys. **10**, 240 (1942); (b) A. A. Frost, R. E. Kellogg, and E. C. Curtis, Rev. Mod. Phys. **32**, 313 (1960); (c) A. A. Frost, R. E. Kellogg, B. M. Gimarc, and J. D. Scargle, J. Chem. Phys. **35**, 827 (1961); (d) B. M. Gimarc and A. A. Frost, Theoret. Chim. Acta **1**, 87 (1963); (e) J. Chem. Phys. **39**, 1698 (1963); (f) D. K. Harriss and A. A. Frost, *ibid.* **40**, 204 (1964).

[2] Yu V. Vorobyev, *Method of Moments in Applied Mathematics* (Gordon and Breach Science Publications, Inc., New York, 1965); (b) F. R. Halpern, Phys. Rev. **107**, 1145 (1957).

III. METHOD OF LOCAL MOMENTS

In this section we develop several methods for calculating approximate energies, based on Eq. (2). We begin heuristically from the standard method of moments. The basic MM equation[2] for the energy in the nth order,[3] given a function ϕ, is

$$\det\begin{vmatrix} 1 & \mathcal{H}_0 & \mathcal{H}_1 & \cdots & \mathcal{H}_{n-1} \\ E & \mathcal{H}_1 & \mathcal{H}_2 & \cdots & \mathcal{H}_n \\ E^2 & \mathcal{H}_2 & \mathcal{H}_3 & \cdots & \mathcal{H}_{n+1} \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ E^n & \mathcal{H}_n & \mathcal{H}_{n+1} & \cdots & \mathcal{H}_{2n-1} \end{vmatrix} = 0, \quad (11)$$

where

$$\mathcal{H}_k \equiv \langle \phi, H^k\phi \rangle / \langle \phi, \phi \rangle. \quad (12)$$

Equation (11) is most simply derived[2,4] from the variational principle with the basis set

$$\{\phi_i = H^{i-1}\phi \mid i=1, 2, \cdots, n\}.$$

The equation for the nth order energy in the method of local moments (MLM) is obtained formally from Eq. (11) by replacing $\mathcal{H}_k$ [Eq. (12)] with its local equivalent

$$\mathcal{H}_k(\mathbf{x}_0) \equiv [H^k\phi(\mathbf{x})/\phi(\mathbf{x})]_{\mathbf{x}=\mathbf{x}_0}, \quad (13)$$

where $\mathbf{x}_0$ is some chosen point in the configuration space of H at which $\phi(\mathbf{x}_0) \neq 0$:

$$\det\begin{vmatrix} 1 & 1 & \mathcal{H}_1(\mathbf{x}_0) & \cdots & \mathcal{H}_{n-1}(\mathbf{x}_0) \\ E & \mathcal{H}_1(\mathbf{x}_0) & \mathcal{H}_2(\mathbf{x}_0) & \cdots & \mathcal{H}_n(\mathbf{x}_0) \\ E^2 & \mathcal{H}_2(\mathbf{x}_0) & \mathcal{H}_3(\mathbf{x}_0) & \cdots & \mathcal{H}_{n+1}(\mathbf{x}_0) \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ E^n & \mathcal{H}_n(\mathbf{x}_0) & \mathcal{H}_{n+1}(\mathbf{x}_0) & \cdots & \mathcal{H}_{2n-1}(\mathbf{x}_0) \end{vmatrix} = 0. \quad (14)$$

This secular equation (14) can be derived as follows:

(1) Let

$$\psi(\mathbf{x}_0) = \sum_{i=1}^{n} c_i H^{i-1}\phi(\mathbf{x}_0). \quad (15)$$

(2) Determine the c_i and E from the n simultaneous equations

$$H^k\psi(\mathbf{x}_0) = E^k\psi(\mathbf{x}_0) \qquad (k=1, 2, \cdots, n). \quad (16)$$

The justification for imposing Eq. (16) is the local-moment lemma. Such a $\psi(\mathbf{x}_0)$ has the property that the first n local moments of H at $\mathbf{x}_0$ are powers of the local energy. With Eq. (15), Eq. (16) becomes

$$\sum_{i=1}^{n} (H^k - E^k) H^{i-1}\phi(\mathbf{x}_0) c_i = 0, \quad (k=1, 2, \cdots, n), \quad (17)$$

which has a nontrivial solution for the c_i if, and only if,

$$\det \mid H^{k+i-1}\phi(\mathbf{x}_0) - E^k H^{i-1}\phi(\mathbf{x}_0) \mid = 0. \quad (18)$$

Divide each element of the determinant in Eq. (18) by $\phi(\mathbf{x}_0)$, and rewrite the determinant as an $(n+1)\times(n+1)$ determinant whose first row is $(1, 0, 0, \cdots, 0)$ and whose first column is $(1, E, E^2, \cdots, E^n)$:

$$\det\begin{vmatrix} 1 & 0 & 0 & \cdots & 0 \\ E & \mathcal{H}_1 - E & \mathcal{H}_2 - E\mathcal{H}_1 & \cdots & \mathcal{H}_n - E\mathcal{H}_{n-1} \\ E^2 & \mathcal{H}_2 - E^2 & \mathcal{H}_3 - E^2\mathcal{H}_1 & \cdots & \mathcal{H}_{n+1} - E^2\mathcal{H}_{n-1} \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ E^n & \mathcal{H}_n - E^n & \mathcal{H}_{n+1} - E^n\mathcal{H}_1 & \cdots & \mathcal{H}_{2n-1} - E^n\mathcal{H}_{n-1} \end{vmatrix} = 0. \quad (18')$$

By adding $\mathcal{H}_{i-1}$ times the first column to the $(i+1)$th column, $i=1, 2, \cdots, n$, one obtains Eq. (14).

Illustrations

The three examples discussed here are chosen to bring out certain aspects of the MLM. Applications to physically more interesting problems, e.g., many-electron systems, are in progress.

First we wish to illustrate that the roots of the MLM secular equation coincide with the exact eigenvalues if the basis is complete. Consider a somewhat artificial case, a spin-$\frac{1}{2}$ particle in a magnetic field **B** pointing in the x direction. The Hamiltonian is

$$H = bS_x, \quad (19)$$

where b lumps together various irrelevant constants, and S_x is the x component of the spin angular momentum. Take $\phi=\alpha$ (α and β are the usual spin functions quantized in the z direction), and assign α and β the arbitrary (i.e., "local") values A and B. Equation

[3] By "nth-order energy" we mean an appropriate root of the secular equation in which the highest power of E is the nth.

[4] R. L. Somorjai, "Method of Moments in Quantum Mechanics" (unpublished); see also S. M. Blinder, Intern. J. Quantum Chem. 1, 271 (1967).

TABLE I. Energies for a harmonic osicllator of frequency $(1+\eta)^{1/2}$ calculated from Eq. (14), with $\phi(x) = \exp(-\frac{1}{2}x^2)$.

Frequency[a] $(1+\eta)^{1/2}$	n	Approximate energies = roots of Eq. (14)											
		$(x_0)^2=0.00$				$(x_0)^2=1.00$				$(x_0)^2=2.00$			
1.1	1	0.50000				0.60500				0.71000			
	4	0.55001	2.7426	b	b	0.54999	2.7440	5.2589	5.9764	0.54996	2.7457	5.2526	b
	8	0.55000	2.7500	4.9501	7.1413	0.55000	2.7500	4.9500	7.1494	0.55000	2.7500	4.9499	7.1454
	Exact[c]	0.55000	2.7500	4.9500	7.1500	0.55000	2.7500	4.9500	7.1500	0.55000	2.7500	4.9500	7.1500
1.5	1	0.50000				1.1250				1.7500			
	4	0.75599	3.1706	b	b	0.74267	3.3963	b	b	0.75018	3.7686	b	b
	8	0.75001	3.7386	b	b	0.75000	3.7494	6.7778	9.4935	0.75003	3.7531	b	b
	Exact	0.75000	3.7500			0.75000	3.7500	6.7500	9.7500	0.75000	3.7500		

[a] The $\phi(x) = \exp(-\frac{1}{2}x)$ is the exact eigenfunction with $E=0.5$ only when $\eta=0$. When $\eta \neq 0$, $\phi(x)$ approximates the eigenfunction with energy $0.5\ (1+\eta)^{1/2}$.

[b] The nth order secular equation sometimes has less than n real roots.

[c] The exact energies are $(n+\frac{1}{2})(1+\eta)^{1/2}$ when $n=0, 2, 4, \cdots$. Only "even" roots are calculated from the secular equation, because $\phi(x)$, $H\phi(x)$, $H^2\phi(x), \cdots$, are all even functions when $\phi(x)$ is even.

(14), with $n=2$, becomes

$$\det \begin{vmatrix} 1 & 1 & \frac{1}{2}bB/A \\ E & \frac{1}{2}bB/A & \frac{1}{4}b^2 \\ E^2 & \frac{1}{4}b^2 & \frac{1}{8}b^3B/A \end{vmatrix} = 0 \tag{20}$$

$$= (E^2-\tfrac{1}{4}b^2)(\tfrac{1}{4}b^2)(1-B^2/A^2). \tag{21}$$

The roots of Eq. (21) are

$$E=\pm\tfrac{1}{2}b, \tag{22}$$

the exact eigenvalues of H (as expected), independent of the values assigned α and β, provided $A^2 \neq B^2$. This example illustrates another aspect of MLM—that it can fail for certain choices of $\mathbf{x}_0$. In this case, the "choice" $A=\pm B$ makes the secular determinant identically zero.

The second example illustrates how the accuracy of the approximate energy is related to the closeness of the initial ϕ to the exact wavefunction. Consider a spin-1 particle whose S_z eigenfunctions are $|1\rangle$, $|0\rangle$, and $|-1\rangle$. Let

$$\phi = |1\rangle + \lambda^{-1}(|0\rangle + |-1\rangle), \tag{23}$$

where λ is a mixing parameter. Take $n=2$ in Eq. (14) (for $n=3$ the basis would be complete), and assign $|1\rangle$, $|0\rangle$, and $|-1\rangle$ the "local values" A, B, and C, respectively. With $H=S_z$, the exact eigenvalue of $|1\rangle$ is 1, whereas the approximate E from Eq. (14) is

$$E = 1-\lambda^{-1}[2BC/(8AC+AB)]+O(\lambda^{-2}). \tag{24}$$

Thus, the error in the approximate energy is of the order of λ^{-1}, which is the same order as the error in ϕ.

For a third example, consider a harmonic oscillator with

$$H = -\tfrac{1}{2}(d/dx)^2+\tfrac{1}{2}(1+\eta)x^2, \tag{25}$$

and take

$$\phi = \exp(-\tfrac{1}{2}x^2). \tag{26}$$

(If η were 0, then ϕ would be an exact eigenfunction with $E=\frac{1}{2}$.) In Table I, the values of E computed from Eq. (14) for several values of x_0, η, and n are listed. Note that for a given n, the computed energies are not too sensitive to the value of x_0. When x_0 was taken to be $\frac{1}{2}\sqrt{2}$, however, the method failed because of difficulties similar to those in the first example when $A^2=B^2$.

IV. METHOD OF LOCAL MOMENTS: GENERALIZATIONS

It is possible to generalize the MLM in two directions. First, more than one starting function can be used; second, the moments can be evaluated at more than one point simultaneously.

Consider first a set of n starting functions $\{\phi_1, \phi_2, \cdots, \phi_n\}$. Let

$$\psi(\mathbf{x}_0) = \sum_{i=1}^{n} c_i\phi_i(\mathbf{x}_0).$$

Require Eq. (2) to hold for $k=1, 2, \cdots, n$. Then the

equation for the nth-order E becomes

$$\det\begin{vmatrix} 1 & \phi_1(\mathbf{x}_0) & \phi_2(\mathbf{x}_0) & \cdots & \phi_n(\mathbf{x}_0) \\ E & H\phi_1(\mathbf{x}_0) & H\phi_2(\mathbf{x}_0) & \cdots & H\phi_n(\mathbf{x}_0) \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \\ E^n & H^n\phi_1(\mathbf{x}_0) & H^n\phi_2(\mathbf{x}_0) & \cdots & H^n\phi_n(\mathbf{x}_0) \end{vmatrix} = 0. \tag{27}$$

[We have multiplied the kth column by $\phi_k(\mathbf{x}_0)$.] This equation could be called a local configuration-interaction secular equation. Notice that the original Eq. (14) is recovered by choosing the special basis functions $\phi_i = H^{i-1}\phi_1$.

Secondly, consider the requirement that Eq. (2) hold not only at $\mathbf{x}_0$, but simultaneously at $\mathbf{x}_1$, and let the number of basis functions $H^{i-1}\phi$ be $2n$. Then the secular determinant has the form

$$\det\begin{vmatrix} (H-E)\phi(\mathbf{x}_0) & (H^2-EH)\phi(\mathbf{x}_0) & \cdots & (H^{2n}-EH^{2n-1})\phi(\mathbf{x}_0) \\ (H^2-E^2)\phi(\mathbf{x}_0) & (H^3-E^2H)\phi(\mathbf{x}_0) & \cdots & (H^{2n+1}-E^2H^{2n-1})\phi(\mathbf{x}_0) \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ (H^n-E^n)\phi(\mathbf{x}_0) & (H^{n+1}-E^nH)\phi(\mathbf{x}_0) & \cdots & (H^{3n-1}-E^nH^{2n-1})\phi(\mathbf{x}_0) \\ (H-E)\phi(\mathbf{x}_1) & (H^2-EH)\phi(\mathbf{x}_1) & \cdots & (H^{2n}-EH^{2n-1})\phi(\mathbf{x}_1) \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ (H^n-E^n)\phi(\mathbf{x}_1) & (H^{n+1}-E^nH)\phi(\mathbf{x}_1) & \cdots & (H^{3n-1}-E^nH^{2n-1})\phi(\mathbf{x}_1) \end{vmatrix} = 0. \tag{28}$$

Similar equations can be derived for the case when the "local moments" are evaluated at an arbitrary number of points.

These two approaches can also be combined. For instance, take the $2n$ basis functions $\{\phi_1, H\phi_1, \cdots, H^{n-1}\phi_1, \phi_2, H\phi_2, \cdots, H^{n-1}\phi_2\}$ and require Eq. (2) to hold at two points, $\mathbf{x}_0$ and $\mathbf{x}_1$, for $k=1, 2, \cdots, n$. These $2n$ simultaneous equations lead to an obvious secular equation for E.

V. DISCUSSION

The main computational advantage of the method of local moments is the absence of integrals. Approximate wavefunctions may be used which would not be suitable for variational calculations because of integral evaluation difficulties, e.g., explicit functions of interparticle coordinates. A second advantage is that the accuracy of the calculated energy can be improved systematically by increasing n in the secular equation [(14), (27), or (28)]. The harmonic-oscillator example, Table I, shows this clearly. In contrast, the main way to increase accuracy in the LEM is to take a larger number of points, which must be chosen somewhat arbitrarily. Moreover, the choice of $\mathbf{x}_0$ is not so crucial as in the LEM. The main advantage of MLM over MM [Eq. (11)] is that in the case of singular Hamiltonians, the higher moments [Eq. (12)] may diverge, whereas the local moments do not.

The method also has disadvantages. There is no variational principle. Although the choice of $\mathbf{x}_0$ is not as crucial as in the LEM, certain values of $\mathbf{x}_0$ might cause the secular determinant to vanish identically (see the illustrations above). Note that the roots of the secular equation can be complex. As n increases, the determinant in Eq. (14) tends toward zero, which can cause computational difficulties. Another disadvantage is the large number of terms in $H^n\phi$ when H is the sum of several terms.

A final disadvantage is the present lack of a suitable convergence test. Suppose $\psi(\mathbf{x}_0)$ satisfies Eqs. (4) and (14). Then,

$$(E-E_1)\psi(\mathbf{x}_0) = \sum_{i=n+1}^{\infty} c_i\chi_i(\mathbf{x}_0)(E_i-E_1) \times \prod_{j=2}^{n}(E_i-E_j)(E-E_j)^{-1}. \tag{29}$$

If E is near E_1, and if the coefficients c_i fall off rapidly as i increases, then

$$|E(n)-E_1| \sim |c_{n+1}(E_{n+1}-E_1)|, \tag{30}$$

where $E(n)$ denotes the nth-order estimate for E. The following *rough* observation can thus be made: If ψ, by choice of the basis functions, can represent an eigenfunction of H accurately, then increasing n increases the accuracy of the calculated energy.

ACKNOWLEDGMENT

It is a pleasure to thank Professor S. F. Boys for a most helpful comment.