

***N*-electron zero-momentum energy expression: A criterion for assessing the accuracy of approximate wave functions**

Ajit J. Thakkar

*Quantum Theory Group, Department of Applied Mathematics, University of Waterloo,
Waterloo, Ontario, Canada N2L 3G1*

Vedene H. Smith, Jr.

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

(Received 3 February 1978)

A derivation and discussion of Armstrong's *N*-electron zero-momentum energy expression is presented. This functional $E_{zm}(\chi)$ is linear in the wave function χ , and thus is easier to compute and more sensitive to wave-function error than the variational upper bound $E_{var}(\chi)$. The smallness of the quantity $\Delta(\chi) = E_{zm}(\chi) - E_{var}(\chi)$ provides an *a priori* criterion for assessment of the accuracy of an approximate wave function. Nontrivial numerical examples are given to illustrate the utility of this criterion.

I. INTRODUCTION

Recent advances in the technology of electronic computation have been paralleled by an enormous increase in the amount of effort devoted to finding approximate solutions of the *N*-electron Schrödinger equation

$$\left(-\frac{1}{2} \sum_{k=1}^N \nabla_k^2 + V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \right) \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = E \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N), \quad (1)$$

where \vec{r}_k is the position vector of the *k*th electron, $V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ is the spin-free external potential in which the electrons move, E is the energy, and $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ is the position-space wave function. Note that atomic units are used throughout this paper. Spin variables are suppressed wherever they play no direct role.

The accuracy of an approximate wave function may be gauged by comparison of calculated expectation values of dynamical variables with experimental results. This approach is limited by the availability and accuracy of experimental data. Moreover it is inapplicable whenever the calculation refers to an experimentally unobserved quantity. Therefore *a priori* criteria for assessing

the accuracy of approximate wave functions are of great interest.

The virial theorem,¹ the cusp conditions for the wave function,² the spherical average of the charge density³ and the intracule function,⁴ local-energy functionals,⁵ and reduced local-energy functionals⁶ have all been utilized for such *a priori* tests. In 1964 Armstrong⁷ derived another *a priori* criterion which unfortunately has been overlooked since that time; perhaps, because of the relative inaccessibility of his work.

Armstrong^{7(a)} examined the Fourier-transformed Schrödinger equation at that point in momentum space where the momentum vector of every electron is equal to zero. He thus obtained a simple energy expression that is *more sensitive* to the error in the wave function than the expectation-value expression. The difference between the energy values computed from these two expressions thus provides an *a priori* criterion for assessing the accuracy of an approximate wave function.

In Sec. II a derivation of this *N*-electron zero-momentum energy expression is presented. Various aspects of this expression are discussed and illustrated with nontrivial numerical examples in Sec. III. These examples also serve as additional tests of the accuracy of a set of compact and accurate explicitly-correlated generator-coordinate wave functions recently constructed^{8,9} for the heliumlike ions.

II. DERIVATION

The integral form of the *N*-electron Schrödinger equation in momentum space may be written as¹⁰

$$\left(E - \frac{1}{2} \sum_{i=1}^N \vec{p}_i \cdot \vec{p}_i \right) \phi(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) = \int d\vec{p}'_1 d\vec{p}'_2 \cdots d\vec{p}'_N W(\vec{p}_1 - \vec{p}'_1, \vec{p}_2 - \vec{p}'_2, \dots, \vec{p}_N - \vec{p}'_N) \phi(\vec{p}'_1, \vec{p}'_2, \dots, \vec{p}'_N), \quad (2)$$

where E is the energy, \vec{p}_k is the momentum vector of the k th electron, and

$$W(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) = (2\pi)^{-3N} \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \exp\left(-i \sum_{k=1}^N \vec{r}_k \cdot \vec{p}_k\right). \quad (3)$$

$\phi(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$ is the momentum-space wave function which is simply the Fourier transform of the position-space wave function $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$. Thus

$$\phi(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) = (2\pi)^{-3N/2} \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \exp\left(-i \sum_{k=1}^N \vec{r}_k \cdot \vec{p}_k\right). \quad (4)$$

and

$$\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = (2\pi)^{-3N/2} \int d\vec{p}_1 d\vec{p}_2 \cdots d\vec{p}_N \phi(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) \exp\left(i \sum_{k=1}^N \vec{r}_k \cdot \vec{p}_k\right). \quad (5)$$

Now consider the case when *all* the momentum vectors vanish, i. e.,

$$\vec{p}_1 = \vec{p}_2 = \cdots = \vec{p}_N = \vec{0}. \quad (6)$$

Under such circumstances, Eq. (2) may be written

$$\begin{aligned} E\phi(\vec{0}, \vec{0}, \dots, \vec{0}) &= \int d\vec{p}'_1 d\vec{p}'_2 \cdots d\vec{p}'_N W(-\vec{p}'_1, -\vec{p}'_2, \dots, -\vec{p}'_N) \phi(\vec{p}'_1, \vec{p}'_2, \dots, \vec{p}'_N) \\ &= (2\pi)^{-9N/2} \int d\vec{p}'_1 d\vec{p}'_2 \cdots d\vec{p}'_N d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N d\vec{r}'_1 d\vec{r}'_2 \cdots d\vec{r}'_N \psi(\vec{r}'_1, \vec{r}'_2, \dots, \vec{r}'_N) \\ &\quad \times V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \exp\left(i \sum_{k=1}^N \vec{p}'_k \cdot (\vec{r}_k - \vec{r}'_k)\right) \\ &= (2\pi)^{-3N/2} \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N d\vec{r}'_1 d\vec{r}'_2 \cdots d\vec{r}'_N \psi(\vec{r}'_1, \vec{r}'_2, \dots, \vec{r}'_N) \\ &\quad \times V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \delta(\vec{r}_1 - \vec{r}'_1) \cdots \delta(\vec{r}_N - \vec{r}'_N) \\ &= (2\pi)^{-3N/2} \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N). \end{aligned} \quad (7)$$

Note that Eq. (4) yields

$$\phi(\vec{0}, \vec{0}, \dots, \vec{0}) = (2\pi)^{-3N/2} \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N). \quad (8)$$

Combining Eqs. (7) and (8) we obtain the desired result

$$E \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N). \quad (9)$$

If the integral on the left-hand side of the above equation is nonzero, then the N -electron zero-momentum energy expression is obtained

$$E = \frac{\int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{\int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_N \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}. \quad (10)$$

The integrals in Eq. (9) are understood to be spin-traced. These integrals are nonzero only for spatially totally symmetric singlet states. Hence the step from Eq. (9) to Eq. (10) is only valid for such states. For all other states, Eq. (9) is trivially satisfied and yields no useful information.

III. DISCUSSION

The energy expression Eq. (10) is a local-energy functional in momentum-space analogous to the Bartlett-Frost local-energy functional⁵ in position-

space

$$E_{\text{BF}}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \frac{H \psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}{\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}, \quad (11)$$

where H is the Hamiltonian operator. The momentum-space local-energy functional has been restricted to a single point in momentum space simply because it is most tractable at that point. Armstrong's alternative derivation^{7(b)} shows a clear relationship between Eqs. (10) and (11) without reference to momentum space: Eq. (10) is essentially an integrated form of Eq. (11).

Let $\chi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ be an approximation to the position-space wave function $\psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$. The variational approximation to the corresponding energy is then given by

$$E_{\text{var}}(\chi) = \int \chi^* H \chi d\tau / \int \chi^* \chi d\tau. \quad (12)$$

This approximation is, in fact, an upper bound to the true energy. Thus,

$$\Delta_{\text{var}}(\chi) = E_{\text{var}}(\chi) - E \geq 0. \quad (13)$$

The N -particle zero-momentum approximation to the energy is given by

$$E_{\text{zm}}(\chi) = \int V \chi d\tau / \int \chi d\tau. \quad (14)$$

This approximation is not a bound and thus the error

$$\Delta_{\text{zm}}(\chi) = E_{\text{zm}}(\chi) - E \quad (15)$$

may be of either sign. Of course for exact wave functions ψ we have

$$\Delta_{\text{var}}(\psi) = \Delta_{\text{zm}}(\psi) = 0. \quad (16)$$

Note that $E_{\text{zm}}(\chi)$ is much easier to compute than $E_{\text{var}}(\chi)$.

It is easy to see that $\Delta_{\text{zm}}(\chi)$ is linear in the wave function error whereas $\Delta_{\text{var}}(\chi)$ is quadratic in the wave function error. Since many expectation-value expressions for operators other than the Hamiltonian are also linear in the wave-function error, $\Delta_{\text{zm}}(\chi)$ should give an indication of the error in such computed properties other than the energy.

If the exact energy E is unavailable, then the quantity

$$\Delta(\chi) = E_{\text{zm}}(\chi) - E_{\text{var}}(\chi) = \Delta_{\text{zm}}(\chi) - \Delta_{\text{var}}(\chi) \quad (17)$$

can be used to approximate $\Delta_{\text{zm}}(\chi)$ because $\Delta_{\text{var}}(\chi)$ can be expected to be much smaller than $\Delta_{\text{zm}}(\chi)$ for most (but not all) reasonable choices of χ . It is important to note that

$$\Delta(\chi) = 0 \quad (18)$$

is a necessary but not sufficient condition that χ be equal to the exact wave function. The "necessary" part of the above statement is obvious from the development so far, and the "not sufficient" part is shown by the following example given by Armstrong.^{7(a)} The simple Kellner approximation¹⁰

$$\chi = \alpha^3 \pi^{-1} \exp[-\alpha(r_1 + r_2)], \quad (19)$$

with

$$\alpha = Z - \frac{5}{16} \quad (20)$$

for the wave function for the ground state of a two-electron ion with nuclear charge Z satisfies Eq. (18), but is obviously not the exact wave function. Armstrong^{7(a)} has given a detailed explanation for this peculiar property of the Kellner function.

Suppose that χ_1 and χ_2 are two different approximations to ψ . Then an order relation between $\Delta_{\text{var}}(\chi_1)$ and $\Delta_{\text{var}}(\chi_2)$ does not imply the same order relation between $\Delta_{\text{zm}}(\chi_1)$ and $\Delta_{\text{zm}}(\chi_2)$. In particular, $\Delta_{\text{var}}(\chi_1) = \Delta_{\text{var}}(\chi_2)$ does not imply $\Delta_{\text{zm}}(\chi_1) = \Delta_{\text{zm}}(\chi_2)$ and $\Delta_{\text{var}}(\chi_1) < \Delta_{\text{var}}(\chi_2)$ does not imply $|\Delta_{\text{zm}}(\chi_1)| < |\Delta_{\text{zm}}(\chi_2)|$.

Tables I and II list values of Δ_{var} and Δ_{zm} for a set of highly accurate explicitly correlated wave functions of the form

$$\chi(r_1, r_2, r_{12}) = (4\pi)^{-1} \sum_{k=1}^L C_k (1 + P_{12}) \times \exp(-\alpha_k r_1 - \beta_k r_2 - \gamma_k r_{12}) \quad (21)$$

recently constructed^{8,9} for the 1^1S and 2^1S states of the heliumlike ions. These tables also list values of the ratios $R = \Delta_{\text{zm}}^2 / \Delta_{\text{var}}$ and Δ / E_{var} . These tables clearly show that Δ_{zm} can be of either sign and that order relations for Δ_{var} do not imply order relations for Δ_{zm} . The facts that $\Delta_{\text{var}} \ll |\Delta_{\text{zm}}|$ in all cases and that in many cases R is of the order

TABLE I. Zero-momentum energy tests for wave functions (Ref. 8) for the ground states of the heliumlike ions. The "exact" energies used are from Ref. 12 for $Z = 1, 2, \dots, 10$ and from Ref. 13 for $Z = 11, 12$. In both Tables I and II the number and letter in the wave-function column indicates the number of terms and the scheme of construction (see Refs. 8 and 9), and the notation $A-n$ means $A \times 10^{-n}$.

Wave function	Z	Δ_{var}	Δ_{zm}	R	Δ / E_{var}
20P	1	1.27-6	4.74-4	0.18	-8.96-4
30P	1	7.50-7	1.87-4	0.047	-3.53-4
60P	1	7.63-8	6.54-4	5.6	-1.24-3
66Z	1	3.09-8	-5.78-5	0.11	1.10-4
66Z	2	1.43-8	4.58-4	15	-1.58-4
45P	3	1.46-7	7.23-4	3.6	-9.92-5
25P	4	1.26-6	-6.26-3	31	4.58-4
25P	5	1.22-6	-6.34-3	33	2.88-4
25P	6	1.25-6	-9.50-3	72	2.93-4
25P	7	1.28-6	-1.29-2	131	2.89-4
25P	8	1.30-6	-1.63-2	205	2.76-4
25P	9	1.55-6	-2.09-2	281	2.76-4
25P	10	4.12-6	8.46-3	17	-9.00-5
20P	11	4.50-6	-7.97-3	14	6.98-5
20P	12	4.00-6	-6.00-2	899	4.39-4

TABLE II. Zero-momentum energy tests for wave functions (Ref. 9) for the 2^1S states of the heliumlike ions. The "exact" energies used are from Ref. 14 for $Z = 2, 3, \dots, 10$ and from Ref. 15 for $Z = 11, 12$. See also the heading to Table I.

Wave function	Z	Δ_{var}	Δ_{zm}	R	Δ/E_{var}
55P	2	2.20-7	1.23-4	0.068	-5.71-5
40P	3	1.32-6	1.06-3	0.85	-2.10-4
25P	4	1.59-5	-1.49-3	0.14	1.64-4
25P	5	8.09-6	-1.04-4	0.001	7.68-6
25P	6	1.52-5	6.40-3	2.7	-3.01-4
25P	7	1.09-5	-1.83-3	0.31	6.31-5
25P	8	1.25-5	2.91-3	0.68	-7.58-5
20P	9	5.00-5	4.91-3	0.48	-9.98-5
20P	10	5.26-5	4.93-3	0.46	-8.09-5
20P	11	5.69-5	6.19-3	0.67	-8.37-5
20P	12	1.76-5	3.70-2	78	-4.24-4

of unity numerically illustrated that E_{zm} is linear in wave-function error, whereas E_{var} is quadratic in wave-function error. The smallness of $|\Delta_{\text{zm}}|$ and Δ/E_{var} provide additional indications of the high accuracy of these wave functions. Further numerical examples were given by Armstrong who tabulated^{7(a)} E_{zm} and E_{var} for three-, six-, and ten-parameter Hylleraas-type wave functions¹⁰ for

the ground states of the helium atom and hydride ion.

In summary, we note that the zero-momentum energy functional $E_{\text{zm}}(\chi)$ provides another *a priori* computationally simple criterion for assessing the accuracy of an approximate wave function and should be more widely used. From its very definition, $E_{\text{zm}}(\chi)$ may be valuable as an indication of the quality of approximate wave functions for the calculation of momentum-space properties which are sensitive to smaller values of \vec{p} , such as the height and curvature of the peak of the Compton profile.¹¹ Since $E_{\text{zm}}(\chi)$ weights larger \vec{r} regions of position space it may be useful^{7(a)} as an indicator of the accuracy to be expected of transition probabilities computed from the dipole-length formula. Finally it may be possible to improve the asymptotic behaviour of approximate wave functions by enforcing the requirement that $\Delta(\chi)$ be small.^{7,8}

ACKNOWLEDGMENTS

Support of this research by the National Research Council of Canada is gratefully acknowledged. Thanks are due Dr. B. H. Armstrong for a copy of Ref. 7(a). One of us (A. J. T.) would like to thank the National Research Council of Canada for a Postdoctoral Fellowship and Professor Ian J. McGee for his generous hospitality at Waterloo.

¹(a) E. A. Hylleraas, *Z. Phys.* **54**, 347 (1929); (b) V. Fock, *ibid.* **63**, 855 (1930); (c) P.-O. Löwdin, *J. Mol. Spectrosc.* **3**, 46 (1959).

²(a) T. Kato, *Commun. Pure Appl. Math.* **10**, 151 (1957); (b) R. T. Pack and W. Byers-Brown, *J. Chem. Phys.* **45**, 556 (1966).

³E. Steiner, *J. Chem. Phys.* **39**, 2365 (1961).

⁴(a) A. J. Thakkar, Ph.D. thesis (Queen's University at Kingston, 1976) (unpublished); (b) A. J. Thakkar and V. H. Smith, Jr., *Chem. Phys. Lett.* **42**, 476 (1976).

⁵(a) J. H. Bartlett, *Phys. Rev.* **51**, 661 (1937); (b) A. A. Frost, *J. Chem. Phys.* **10**, 240 (1942); (c) A. A. Frost, R. E. Kellog, and E. C. Curtis, *Rev. Mod. Phys.* **32**, 313 (1960).

⁶(a) G. F. Thomas, F. Javor, and S. M. Rothstein, *J. Chem. Phys.* **64**, 1574 (1976); (b) F. Javor, G. F. Thomas, and S. M. Rothstein, *Int. J. Quantum Chem.* **11**, 59 (1977); (c) Reduced local-energy functionals have also been introduced in connection with the N -representability problem. See H. Nakatsuji, *Phys. Rev. A* **14**, 41 (1976).

⁷(a) B. H. Armstrong, Lockheed Missiles and Space Company Technical Report Physics 6-74-64-26, 1964 (un-

published); (b) B. H. Armstrong, *Bull. Am. Phys. Soc.* **9**, 401 (1964).

⁸A. J. Thakkar and V. H. Smith, Jr., *Phys. Rev. A* **15**, 1 (1977).

⁹A. J. Thakkar and V. H. Smith, Jr., *Phys. Rev. A* **15**, 16 (1977).

¹⁰See, for example, H. A. Bethe, and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).

¹¹See, for example, R. Benesch and V. H. Smith, Jr., in *Wave Mechanics—The First Fifty Years*, edited by W. C. Price, S. S. Chissick, and T. Ravensdale, (Butterworths, London, 1973); and L. Mendelsohn and V. H. Smith, Jr., in *Compton Scattering—The Investigation of Electron Momentum Distributions*, edited by B. G. Williams (McGraw-Hill, London, 1977).

¹²K. Frankowski and C. L. Pekeris, *Phys. Rev.* **146**, 86 (1966).

¹³J. Midtdal and K. Aashamar, *Phys. Norv.* **2**, 99 (1967).

¹⁴Y. Accad, C. L. Pekeris, and B. Schiff, *Phys. Rev. A* **4**, 516 (1971).

¹⁵J. Midtdal, G. Lyslo, and K. Aashamar, *Phys. Norv.* **3**, 163 (1969).