PHYSICAL REVIEW A VOLUME 40, NUMBER 10 NOVEMBER 15, 1989

Brief Reports

Brief Reports are short papers which report on completed research which, while meeting the usual **Physical Review** *standards of scientific quality, does not warrant a regular article. (Addenda to papers previously published in the* **Physical Review** *by the same authors are included in Brief Reports.) A Brief Report may be no longer than 3½ printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Lower bound on the ground-state energies of atoms and molecules by variational quantum Monte Carlo methods

Lawrence R. Pratt
Chemical and Laser Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

(Received 30 January 1989)

It is pointed out that the rms fluctuation of the local energy encountered in variational Monte Carlo calculations, together with the expected energy, can be used to produce a nontrivial lower bound on the ground-state energies of atoms and molecules. This lower bound has the desirable properties of general accessibility (via Monte Carlo calculations) and linear sensitivity to deviations of the trial wave function from the exact wave function. These qualities of accessibility and sensitivity are demonstrated with numerical data obtained from recent Monte Carlo calculations on the helium atom and the hydride ion.

It is an often noted fact that most quantum Monte Carlo methods become statistically more efficient as the trial wave function more accurately describes the ground-state many-body wave function of the system under study.[1-5] This is true for standard variational calculations because the variance of the sampled quantity, the local energy to be defined below, is zero when the trial wave function equals the ground-state wave function and is expected to approach zero as the trial wave function approaches the ground-state wave function. It is clear that a variational calculation could be formulated upon the principle that the fluctuation of the local energy be as small as possible rather than upon the principle that the expected energy be as low as possible.[6-8] Here it is pointed out that the expected energy less the rms fluctuation of the local energy typically provides a lower bound on the true ground-state energy. The qualifier "typically" means that exceptional cases are possible. However, the conditions leading to such exceptions are pretty simple. In the typical calculations on atoms and molecules, i.e., calculations on the ground states of bound systems of finite spatial extent, it is not expected that the exceptions will be troublesome.

The importance of these results lies in the general accessibility of this lower bound and its sensitivity as a test of the quality of a wave function. The numerical results given exemplify these two aspects. With respect to accessibility, we are able to use previously obtained data to formulate lower bounds which were not recognized in that previous work. It is important to note that the bound discussed here does not require explicit knowledge of the energy of the first excited state as does the well-known lower bound due to Temple,[9] which has been previously utilized by, for example, Kinoshita.[10] Additional information of that type cannot be expected to be routinely available. When it is available, a more stringent bound on the ground-state energy might be formulated. However, a bound that does not require information extraneous to the wave function under consideration and that sensitively highlights the inaccuracies of that wave function is to be preferred as a test of the quality of the ground-state wave function. The examples presented clearly display this desired sensitivity: The lower bound discussed here is more useful as a test of the quality of wave function than is the customary Rayleigh-Ritz upper bound. This provides a helpful perspective on the success of the recent calculations of Umrigar, Wilson, and Wilkins.[8] An analytical explanation of the observed sensitivity of this lower bound is noted below.

The following notation will be used to describe these results. Denote by $\langle \Psi | \mathbf{R} \rangle$ a trial wave function under consideration with $\mathbf{R}$ a point in the configuration space of the system. The Rayleigh-Ritz upper bound on the ground-state energy ε_0 is then expressed as

$$\frac{\langle \Psi | \mathcal{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \equiv \langle \mathcal{H} \rangle \geq \varepsilon_0 , \tag{1}$$

in which $\mathcal{H}$ denotes the Hamiltonian for the system. Variational quantum Monte Carlo approaches[11] estimate the left-hand side of this inequality by introducing the local energy

$$\varepsilon(\mathbf{R})\equiv\frac{\langle\Psi|\mathcal{H}|\mathbf{R}\rangle}{\langle\Psi|\mathbf{R}\rangle}\ . \tag{2}$$

The Metropolis Monte Carlo algorithm is then used to sample the configurations **R** according to the probability density

$$P(\mathbf{R})\equiv\frac{|\langle\Psi|\mathbf{R}\rangle|^2}{\langle\Psi|\Psi\rangle}\ . \tag{3}$$

For a sample of size n the desired value $\langle\mathcal{H}\rangle$ is estimated by

$$E\{\langle\mathcal{H}\rangle\}=\frac{1}{n}\sum_{j=1}^{n}\varepsilon(\mathbf{R}_j)\ . \tag{4}$$

Here $E\{\cdots\}$ means estimate of $\cdots$.

The alternative bound considered here uses the variance σ^2 defined by

$$\sigma^2\equiv\langle\mathcal{H}^2\rangle-\langle\mathcal{H}\rangle^2\ . \tag{5}$$

It was established some time ago that the band $\langle\mathcal{H}\rangle\pm\sigma$ must contain at least one eigenvalue of $\mathcal{H}$.[12-14] If the ground-state eigenvalue ε_0 is the nearest eigenvalue to $\langle\mathcal{H}\rangle$, then $\langle\mathcal{H}\rangle-\sigma$ provides a lower bound on ε_0. This lower bound will therefore be obtained if the trial wave function $\langle\Psi|\mathbf{R}\rangle$ is sufficiently accurate and if the gap between ε_0 and the next higher eigenvalue ε_1, is sufficiently large. These conditions are met often enough in applications to atoms and molecules that this lower bound typically should provide useful information. In that case the true ground-state energy must lie between $\langle\mathcal{H}\rangle$ and $\langle\mathcal{H}\rangle-\sigma$. Note further that $\langle\mathcal{H}\rangle-\sigma$ is a nontrivial lower bound in that it approaches the ground-state energy as $\langle\Psi|\mathbf{R}\rangle$ approaches the exact ground-state wave function.

This lower bound has not been put to much practical use.[15,16] The most likely reason for this is that $\langle\mathcal{H}^2\rangle$ is not routinely accessible in most numerical approaches. Within the Monte Carlo calculations, in contrast, an estimate of $\langle\mathcal{H}^2\rangle$ is always available. This can be recognized by writing

$$\frac{\langle\Psi|\mathcal{H}^2|\Psi\rangle}{\langle\Psi|\Psi\rangle}=\frac{\int d\mathbf{R}\,|\langle\Psi|\mathbf{R}\rangle|^2\left|\frac{\langle\Psi|\mathcal{H}|\mathbf{R}\rangle}{\langle\Psi|\mathbf{R}\rangle}\right|^2}{\int d\mathbf{R}\,|\langle\Psi|\mathbf{R}\rangle|^2}\ . \tag{6}$$

The ratio in the numerator is just the local energy $\varepsilon(\mathbf{R})$. Therefore

$$E\{\langle\mathcal{H}^2\rangle\}=\frac{1}{n}\sum_{j=1}^{n}\varepsilon^2(\mathbf{R}_j)\ . \tag{7}$$

The same sample of configurations can be used for both Eqs. (4) and (7). From those results an estimate of σ can be formed from Eq. (5).

Recently, variational Monte Carlo calculations of just the sort sketched above have been presented for several light atoms with special emphasis on an efficient optimization of electron wave functions.[8] The data obtained there and the unpublished quantum Monte Carlo results on the helium atom contained in Ref. 17 allow us to demonstrate both the accessibility and the sensitivity of the bound discussed above. The combined results of Refs. 8 and 17 were used to prepare the upper and lower bounds shown in Fig. 1. Notice that the upper bounds appear to converge more rapidly than do the lower bounds. For example, the upper bounds change rather slowly for changes of the wave function among functions c through k. However, the lower bounds show that functions c through g are less accurate than are functions h through k. This supports McDowell's suggestion that the fluctuation in the local energy is a key test of the quality of a wave function.[3] This can be understood analytically by noting that the lower bound differs from the ground-state energy at linear order in the deviation of the trial wave function from the exact wave function. In contrast, the upper bound differs from the ground-state energy first at quadratic order. It can be concluded that the upper bound more quickly gives a close prediction of the ground-state energy whereas the lower bound is to be preferred as a figure of merit for a trial wave function. Wave functions that are optimized to give a reasonable lower bound can be expected to provide an accurate expectation value for the energy. It is interesting to note further that the least value of σ is known *a priori*. Therefore it can provide an absolute scale for the relative improvement achieved by modification of a wave function.

The hydride ion H^- can be considered a second example. Variational quantum Monte Carlo calculations were

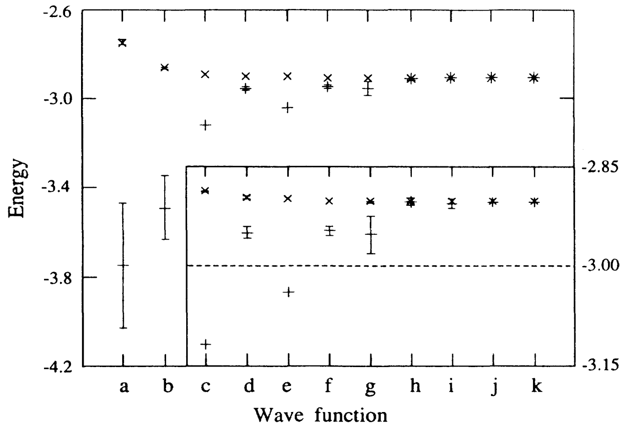

FIG. 1. Upper and lower bounds on the ground-state energy of the helium atom obtained from variational quantum Monte Carlo calculations. Energies are in hartree units. Wave functions c, e, and k are functions (2), (3), and (4) of Ref. 8. A statistical uncertainty was not reported for the rms local energy fluctuation for those functions so no error bars are provided for the lower bounds shown in those cases. All other results shown are taken from Ref. 17. Those wave functions are as follows: a, the hydrogenic wave function $\langle\mathbf{R}|\Psi\rangle\propto\exp[-2(r_1+r_2)][\alpha(1)\beta(2)-\alpha(2)\beta(1)]$; b, the Hartree-Fock wave function of Clementi and Roetti, Ref. 19; d, function 13 of Green, *et al.*, Ref. 20; f, function 15 of Green *et al.*, Ref. 20; g, the six-term function of Schwarz, Ref. 21; h, the ten-term function of Kinoshita, Ref. 10; i, the 13-term function of Schwarz, Ref. 21; j, the 18-term function of Kinoshita, Ref. 10.

reported for this species in Refs. 2 and 8. The calculation of Ref. 2 was repeated for the Chandrasekhar wave function[18] to obtain upper and lower bounds on the ground-state energy in that case. The results are $-0.5260(3)$ and $-0.610(3)$ hartrees. The correlated wave functions of Ref. 8 provide the following bounds on the ground-state energy of H^-: $[-0.5155(3), -0.5975]$, $[-0.5199(2), -0.5899]$, and $[-0.527751(3), -0.5298]$, respectively, for functions (2), (3), and (4) of that work. (A standard error was not reported for the rms local-energy fluctuation for those functions so no statistical uncertainty is given here for these lower bounds.) These results exemplify the possibility that the wave function which yields the lowest expected energy compared to several other wave functions may yet predict significantly less accurate values for other properties than does another of the wave functions under consideration. The Chandrasekhar function yields a remarkably accurate upper bound. It is a rather simple function and constructed on a physical basis to give a low energy. However, the lower bound indicates that considerable improvement is possible in describing the electron wave function of the H^- ion. Although the expected energy of function (2) here is higher than that of the Chandrasekhar function, it is likely to be preferable for purposes other than the prediction of the electronic energy. In such a case, the lower bound discussed here is especially helpful.

The foregoing results indicate an important advantage of Monte Carlo methods for the analysis of explicitly correlated wave functions. These results also indicate that the determination of σ and both upper and lower bounds can help considerably in pursuing variational quantum Monte Carlo calculations where the necessity of obtaining a compact description of a correlated wave function and of optimization with noisy data are often important concerns. Moreover, it is clear that a low value of σ is more directly relevant to the utility of these wave functions in providing importance sampling functions in more complicated quantum Monte Carlo methods than is a low value of $\langle \mathcal{H} \rangle$.

I thank Keith McDowell for allowing me to use the results of his unpublished Monte Carlo study of the helium atom.

---

[1] J. D. Doll, Chem. Phys. Lett. **81**, 335 (1981).

[2] K. McDowell and J. D. Doll, Chem. Phys. Lett. **82**, 127 (1981).

[3] K. McDowell, Int. J. Quantum. Chem. **15**, 177 (1981).

[4] J. W. Moskowitz and K. E. Schmidt, in *Proceedings of NATO-ARW on Monte Carlo Methods in Quantum Physics*, edited by M. H. Kalos (U.S. GPO, Washington, D.C., 1982); P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, J. Chem. Phys. **77**, 5593 (1982); N. C. Handy, R. J. Harrison, P. J. Knowles, and H. F. Schaefer III, J. Phys. Chem. **88**, 4852 (1984); R. N. Barnett, P. J. Reynolds, and W. A. Lester, *ibid.* **91**, 2004 (1987).

[5] M. H. Kalos and P. A. Whitlock, *Monte Carlo Methods, Volume I: Basics* (Wiley, New York, 1986), pp. 93, 94, and 166.

[6] A. A. Frost, J. Chem. Phys. **10**, 240 (1942).

[7] J. H. Bartlett, Phys. Rev. **98**, 1067 (1955).

[8] C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, Phys. Rev. Lett. **60**, 1719 (1988).

[9] G. Temple, Proc. R. Soc. London Ser. A **119**, 276 (1928).

[10] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[11] For example, see D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer-Verlag, New York, 1979), Chap. 4.

[12] D. H. Weinstein, Proc. Natl. Acad. Sci. U.S.A. **20**, 529 (1934).

[13] J. K. L. MacDonald, Phys. Rev. **46**, 828 (1934).

[14] A. F. Stevenson, Phys. Rev. **53**, 199 (1938).

[15] J. H. Bartlett, Jr., Phys. Rev. **51**, 661 (1937).

[16] A. F. Stevenson and M. F. Crawford, Phys. Rev. **54**, 375 (1938).

[17] K. McDowell (unpublished). McDowell considered eight rather different wave functions for the helium atom ranging from a simple hydrogenic function to a highly correlated Hylleraas function. Using the Metropolis algorithm, he estimated both the expected energy and the rms fluctuation of the local energy.

[18] S. Chandrasekhar, Astrophys. J. **100**, 176 (1944).

[19] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[20] L. C. Green, S. Matsushima, C. Stephens, E. K. Kolchim, M. M. Kohler, Y. Wong, B. B. Baldwin, and R. J. Wisner, Phys. Rev. **112**, 1187 (1958).

[21] H. M. Schwarz, Phys. Rev. **103**, 110 (1956).