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Citation: [The Journal of Chemical Physics](#) **112**, 2650 (2000); doi: 10.1063/1.480839

View online: <https://doi.org/10.1063/1.480839>

View Table of Contents: <http://aip.scitation.org/toc/jcp/112/6>

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Optimization of quantum Monte Carlo wave functions using analytical energy derivatives

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(Received 4 October 1999; accepted 9 November 1999)

An algorithm is proposed to optimize quantum Monte Carlo (QMC) wave functions based on Newton's method and analytical computation of the first and second derivatives of the variational energy. This direct application of the variational principle yields significantly lower energy than variance minimization methods when applied to the same trial wave function. Quadratic convergence to the local minimum of the variational parameters is achieved. A general theorem is presented, which substantially simplifies the analytic expressions of derivatives in the case of wave function optimization. To demonstrate the method, the ground-state energies of the first-row elements are calculated. © 2000 American Institute of Physics. [S0021-9606(00)30605-5]

I. INTRODUCTION

Quantum Monte Carlo (QMC) is a powerful method of solving the Schrödinger equation. QMC treats many-body correlation in an efficient and flexible way, enabling highly accurate studies of atoms, small molecules, and clusters.¹⁻³ A high-quality trial wave function is crucial to the calculation, since the trial function determines the ultimate accuracy one can achieve in variational Monte Carlo (VMC) and fixed-node diffusion Monte Carlo, and trial function quality dramatically affects the efficiency of the computation.

An algorithm which efficiently and reliably optimizes wave functions is a critical tool for VMC calculations. One straightforward approach for improving the VMC wave function is to perform energy minimization, in which the variational parameters are altered with the goal of lowering the expectation value of the energy. This approach is complicated in VMC because of the uncertainties associated with stochastic sampling. In order to determine whether a new set of parameters yields a lower energy than the current set, one needs to sample a large number of configurations to ensure that the energy difference between the two sets of parameters is actually larger than the energy error bars. Correlated sampling methods are frequently performed to improve the efficiency of energy minimization. Typically, the energy is calculated using identical sampling points in configuration space for two trial wave functions which differ by a single parameter. The process is repeated for each parameter, and steepest-descent techniques are commonly used for parameter updating.⁴ This correlated sampling approach requires a significant amount of memory (to store data for every sampling point) and the numerical differentiation $\Delta E/\Delta c$ requires many extra evaluations of the local energy. For systems with a large number of parameters, numerical evaluation of the required derivatives becomes computationally intractable. Analytical energy derivative techniques are

very seldom used in current VMC calculations. We will concentrate on this in the following sections.

A successful alternative approach has been developed which focuses on lowering the variance of the local energy, $\hat{H}\Psi/\Psi$.⁵ If the wave function Ψ were the exact ground eigenstate, the local energy would be a constant with a variance of zero. A major strength of the variance minimization approach is that the quantity to be minimized has a minimum value which is known *a priori* (unlike energy minimization). This idea has been implemented in various ways and has recently become a nearly universal approach in VMC wave function optimizations. Typically, one calculates first derivatives of the local energy variance analytically. Steepest-descent techniques^{6,7} or a combination of analytic first derivatives with approximate expressions for the second derivatives are then used for wave function variance reduction (a least-squares fit).⁸⁻¹⁰ Although variance methods have the remarkable strength of an *a priori* minimum value of zero, it is much harder to compute the first and second derivatives of the variance analytically compared to variational energy methods. Therefore, approximate analytical derivatives beyond the first order are used in real calculations, and to our knowledge the validity of these approximations has not been discussed within the scope of VMC wave function optimization. It is important to point out that the "direction sets" minimum-searching methods, such as steepest descent and conjugate gradient, are not efficient for wave function optimization in VMC, because these line-minimization techniques require at least one order of magnitude more evaluation of local energy along the search directions. Moreover, variance minimization is actually an indirect method, since a smaller variance does not necessarily correspond to a lower energy, and the main goal of variational methods such as VMC is the lowest possible upper bound to the energy.

Correlated sampling can be used (instead of analytic derivatives) to lower the variance of the local energy. One excellent version of this idea is known as the fixed-sample method.¹¹ In this approach, the sampling points for the ob-

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jective function (variance of the local energy in this case) are fixed during the optimization procedure, which makes it possible to reduce stochastic noise during the optimization. In addition, it has been observed from a few preliminary calculations that the number of configurations sufficient for parameter updating does not increase rapidly with system size.¹¹ The use of very complex trial correlation functions has yielded highly accurate energies for a few first-row atoms.^{11,12} However, this fixed-sample procedure can have problems if the variational parameters affect the nodes, since the density ratio of the current and initial trial wave functions diverges frequently in the area around the nodes of the trial wave function. Even worse, this density ratio increases exponentially with the size of the system.¹³ Although manually setting an upper bound for the weights or introducing a nodeless sampling probability density function can overcome the singularities in the fixed distribution,¹⁴ a general and appropriate form for the positive definite functions is still unavailable. In addition, the variational energy from fixed-sample calculations can be sensitive to the choice of reference energy, sample size, and convergence criteria.¹⁵

The method we present involves updating the variational parameters to lower the energy expectation value, guided by the force vectors and Hessian matrix of the variational energy with respect to variational parameters. Generally it converges quadratically, making it more efficient than the steepest-descent or quasi-Newton techniques employed in the variance minimization procedure.^{6,8} In most cases, the best set of parameters can be obtained after only one or two iterations. Beginning with an identical trial wave function and the same variational parameters, the correlation energies obtained from our method are significantly better than results in the literature.⁹ With this approach, we also demonstrate the ability to optimize a wave function with a large number of parameters. All of the data are collected and compared in Sec. IV.

II. VMC AND OPTIMIZATION ALGORITHM

Variational Monte Carlo allows us to take our physical insights and construct a trial wave function Ψ_T containing a set of variational parameters $\{c_m\}$. The parameters are varied with the goal of reducing the energy expectation value. In VMC, the true ground-state energy is bounded by the Raleigh–Ritz quotient

$$E_0 \leq E_T(\{c_m\}) = \frac{\int \Psi_T^*(\{c_m\}) \hat{H} \Psi_T(\{c_m\}) d\tau}{\int \Psi_T^*(\{c_m\}) \Psi_T(\{c_m\}) d\tau} \\ = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{\alpha=1}^N (E_L)_\alpha,$$

where $E_L \equiv \hat{H} \Psi_T / \Psi_T$ is called the local energy and α is a configuration-space point, visited with relative probability $\Psi_T^* \Psi_T$, the density of the trial wave function at α .

In a bound molecular system with fixed nuclei, the non-relativistic Hamiltonian

$$\hat{H} = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_{i,l} \frac{Z_l}{r_{il}} + \sum_{i<j} \frac{1}{r_{ij}},$$

has time-reversal symmetry. (Note that capital letter subscripts refer to nuclei and lower-case letters refer to electrons.) Therefore, the true ground-state wave function of this class of Hamiltonian can generally be constructed without an imaginary part, i.e.,

$$\Psi_T^*(\{c_m\}) = \Psi_T(\{c_m\}).$$

In this case, the expectation value of the energy and the first derivative of energy with respect to a variational parameter can be written as

$$E = \frac{\int \Psi \hat{H} \Psi d\tau}{\int \Psi^2 d\tau}, \\ \frac{\partial E}{\partial c_m} = \frac{1}{\int \Psi^2 d\tau} \left(\int \frac{\partial \Psi}{\partial c_m} \hat{H} \Psi d\tau + \int \Psi \hat{H} \frac{\partial \Psi}{\partial c_m} d\tau \right) \\ - \frac{1}{(\int \Psi^2 d\tau)^2} \int \Psi \hat{H} \Psi d\tau \int 2\Psi \frac{\partial \Psi}{\partial c_m} d\tau. \quad (1)$$

Because

$$\int \frac{\partial \Psi}{\partial c_m} \hat{H} \Psi d\tau = \int \Psi \hat{H} \frac{\partial \Psi}{\partial c_m} d\tau,$$

for real wave functions, we simplify Eq. (1) and obtain

$$\frac{\partial E}{\partial c_m} = \frac{2}{\int \Psi^2 d\tau} \int \Psi^2 \left(\frac{\hat{H} \Psi}{\Psi} \right) \left(\frac{\partial \Psi}{\Psi} \right) d\tau \\ - \frac{2}{(\int \Psi^2 d\tau)^2} \int \Psi^2 \frac{\hat{H} \Psi}{\Psi} d\tau \int \Psi^2 \frac{\partial \Psi}{\Psi} d\tau \\ = \lim_{N \rightarrow \infty} \frac{2}{N} \sum_{\alpha=1}^N \{ (E_L \times \Psi'_{ln,m})_\alpha - E \times (\Psi'_{ln,m})_\alpha \}, \quad (2)$$

where we define

$$\Psi'_{ln,m} \equiv \frac{\partial \ln \Psi}{\partial c_m} = \frac{\partial \Psi}{\Psi}.$$

We notice that performing the finite sums for different terms with the same configuration samplings can improve computational efficiency, reducing the fluctuations in the sense of correlated sampling.

Similarly, one can compute the second derivatives of variational energy with respect to variational parameters as

$$\frac{\partial^2 E}{\partial c_m \partial c_n} = \lim_{N \rightarrow \infty} \frac{2}{N} \sum_{\alpha=1}^N \left\{ (E_L \times \Psi''_{ln,m,n})_\alpha - E \times (\Psi''_{ln,m,n})_\alpha \right. \\ + 2[(E_L \times \Psi'_{ln,m} \times \Psi'_{ln,n})_\alpha - E \times (\Psi'_{ln,m} \times \Psi'_{ln,n})_\alpha] \\ - (\Psi'_{ln,m})_\alpha \times \frac{\partial E}{\partial c_n} - (\Psi'_{ln,n})_\alpha \times \frac{\partial E}{\partial c_m} \\ \left. + (\Psi'_{ln,m} \times E'_{L,n})_\alpha \right\},$$

where

TABLE I. Optimized ground-state wave function and variational energy (with error bar and correlation energy percentage) for atoms He to C.

<i>m</i>	<i>n</i>	<i>o</i>	He	Li	Be	B	C
0	0	1	0.250 000 0	0.250 000 0	0.250 000 0	0.250 000 0	0.250 000 0
0	0	2	−0.009 456 4	0.014 387 7	0.197 768 7	0.059 437 9	−0.141 321 8
0	0	3	0.121 467 1	0.276 178 6	−0.839 626 1	−0.632 011 8	−0.128 510 5
0	0	4	−0.139 980 9	−0.522 510 3	0.0631 475 6	0.044 429 8	−0.220 271 9
2	0	0	0.256 969 3	−0.062 574 3	−0.342 820 4	−0.240 258 3	−0.126 957 9
3	0	0	−0.131 696 8	0.194 267 7	1.326 668 6	1.001 928 2	0.532 618 0
4	0	0	−0.848 719 7	−0.549 075 9	−2.168 874 1	−1.825 119 0	−1.256 621 0
2	2	0	−1.260 899 4	−0.523 501 0	−1.118 734 8	−1.033 356 5	−0.891 877 1
2	0	2	0.868 342 9	0.633 604 7	2.186 205 6	1.977 633 2	1.638 829 2
	Energy	(Ha)	−2.9032 22(3)	−7.474 98(5)	−14.641 3(2)	−24.620 6(3)	−37.805 4(3)
	Correlation	(%)	99	93	72	73	75
	Energy(Ref. 9)	(Ha)	−2.902 9(1)	−7.4731(6)	−14.633 2(8)	−24.611 3(8)	−37.795 6(7)
	Correlation(Ref. 9)	(%)	98	89	64	66	68
	Energy-42	(Ha)	−2.903 717(8)	−7.47722(4)	−14.647 5(1)	−24.625 7(1)	−37.811 6(2)
	Correlation-42	(%)	100	98	79	77	79

$$\Psi''_{\ln,m,n} = \frac{\partial^2 \ln \Psi}{\partial c_m \partial c_n},$$

and

$$E'_{L,n} = \frac{\partial E_L}{\partial c_n}.$$

We perform a standard Metropolis walk with importance sampling for E and its first and second derivatives. This gives numerical values for the force vector \mathbf{b} and Hessian matrix \mathbf{H} , which are defined as

$$\mathbf{b} = \left(\frac{\partial E}{\partial c_m} \right)$$

and

$$\mathbf{H} = \left(\frac{\partial^2 E}{\partial c_m \partial c_n} \right).$$

The parameters are then updated according to

$$\mathbf{c}_{\text{next}} = \mathbf{c}_{\text{cur}} - \mathbf{H}^{-1} \cdot \mathbf{b},$$

until converged. Here, \mathbf{c}_{cur} and \mathbf{c}_{next} stand for the current and next values of the trial parameter set, respectively.

III. THEOREM OF LOCAL OBSERVABLE QUANTITY DERIVATIVE

We now demonstrate that the expectation value of the first derivative of the local value $\mathcal{O}_L \equiv \hat{\mathcal{O}}\Psi/\Psi$ of any Hermitian operator $\hat{\mathcal{O}}$ with respect to any real parameter c in any real wave function Ψ is always zero, i.e.,

$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{\alpha=1}^N \left(\frac{\partial \mathcal{O}_L}{\partial c} \right)_{\alpha} \equiv 0. \quad (3)$$

Explicitly, the left-hand side of Eq. (3) is

$$\begin{aligned} & \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{\alpha=1}^N \left\{ \frac{\partial \left(\frac{\hat{\mathcal{O}}\Psi}{\Psi} \right)}{\partial c} \right\}_{\alpha} \\ &= \frac{1}{\int \Psi^2 d\tau} \int \Psi^2 \frac{\partial \left(\frac{\hat{\mathcal{O}}\Psi}{\Psi} \right)}{\partial c} d\tau \\ &= \frac{1}{\int \Psi^2 d\tau} \int \left[\Psi \hat{\mathcal{O}} \frac{\partial \Psi}{\partial c} - \frac{\partial \Psi}{\partial c} \hat{\mathcal{O}} \Psi \right] d\tau = 0. \end{aligned}$$

This theorem explains the simplicity of Eq. (2): the first-order change of expectation value with respect to a change of parameter comes only from the change of wave function and the Metropolis sampling weights, not from the change of the quantity (e.g., the local energy).

IV. APPLICATIONS AND DISCUSSION

To test the performance of this new analytic energy minimization scheme, a well-known trial wave function^{9,16} is used in the calculations. Explicitly, the trial wave function is expressed as

$$\Psi_T = D^\dagger D^\downarrow F$$

$$F = \exp \left(\sum_{i,l \leq j} U_{lij} \right),$$

$$U_{lij} = \sum_k^{N_I} c_{kl} (\bar{r}_{il}^m r_{jl}^n + \bar{r}_{jl}^m r_{il}^n) \bar{r}_{ij}^o,$$

$$\bar{r}_{il} = \frac{b_l r_{il}}{1 + b_l r_{il}},$$

$$\bar{r}_{ij} = \frac{d_l r_{ij}}{1 + d_l r_{ij}},$$

where D^\dagger and D^\downarrow are the Hartree–Fock up-spin and down-spin Slater determinants in a converged Slater type orbital (STO) basis set,¹⁷ and F is a positive correlation wave func-

TABLE II. Optimized ground-state wave function and variational energy (with error bar and correlation energy percentage) for atoms N to Ne.

m	n	o	N	O	F	Ne
0	0	1	0.250 000 0	0.250 000 0	0.250 000 0	0.250 000 0
0	0	2	-0.265 744 3	-0.372 776 7	-0.414 183 0	-0.471 558 9
0	0	3	0.190 686 4	0.467 019 3	0.598 802 0	0.723 079 2
0	0	4	-0.425 218 6	-0.665 306 3	-0.786 171 8	-0.880 226 8
2	0	0	-0.031 499 4	0.035 455 2	0.087 926 0	0.069 032 8
3	0	0	0.234 384 2	0.158 126 1	-0.012 386 9	0.027 063 6
4	0	0	-0.931 422 4	-0.872 373 4	-0.639 209 7	-0.668 939 1
2	2	0	-0.911 104 5	-1.073 630 2	-1.136 846 2	-1.177 452 6
2	0	2	1.521 910 5	1.598 573 4	1.541 888 6	1.560 600 5
Energy			(Ha) -54.547 7(3)	-75.016 8(1)	-99.679 2(2)	-128.883 2(1)
Correlation			(%) 78	80	84	86
Energy (Ref 9)			(Ha) -54.539 0(6)	-75.010 9(4)	-99.668 5(5)	-128.877 1(5)
Correlation (Ref 9)			(%) 73	78	80	85
Energy-42			(Ha) -54.556 3(2)	-75.027 0(1)	-99.691 2(2)	-128.891 0(2)
Correlation-42			(%) 82	84	88	88

tion. The m_{kl} , n_{kl} , and o_{kl} are taken to be integers. All of the parameters c_{kl} , b_I , and d_I can be optimized to obtain the lowest energy.

With our method, a configuration size consisting of 200 000 sampling points is normally enough for satisfactory optimization for the first-row atoms. Typically, one or two iterations are sufficient for convergence, requiring about 50 CPU h on an SGI 90 MHz R8000 processor. Electrons are moved one by one with a time step chosen to maintain an acceptance ratio of 80%. In order to generate one *independent* sample point, a block size of 20 sequential steps is used.

To make a comparison with the variance minimization method, we choose the same set of nine parameters as Schmidt and Moskowitz⁹ with all zeros as initial values. We also obey their constraints, enforcing the unlike-spin electron-electron cusp condition and setting b_I and d_I to unity. The optimized wave function and energy are shown in Tables I and II. The calculated results with our method are noticeably better for all first-row elements, especially for the so-called $2s-2p$ near-degeneracy atoms^{9,18} Be, B, and C. Approximately 10% more correlation energy is recovered by our analytic energy derivative method.

To demonstrate the power of our analytic energy minimization approach more fully, we optimize a 42-parameter wave function, starting from the nine-parameter trial function discussed above. We use all terms with $m+n \leq 4$ combined with $o \leq 3$, $m=n=0$ with $o=4$, and all terms with $m+n > 4$ and $m \leq 4$, $n \leq 4$ with $o=0$. The same cusp, b_I , and d_I constraints were obeyed.

It is also interesting to note that in a recent VMC calculation for atoms Be, B, and C,¹⁸ the use of additional Slater determinants enabled the authors to recover an amount of correlation energy similar to ours. Our current work demonstrates that this $2s-2p$ near-degeneracy effect for the first-row atoms accounts for less than 25% of the correlation energy.

In a typical optimization procedure with this energy derivative method, the energy value and its associated error bar decrease with the first (and possibly second) parameter moves. After that, the forces are much smaller than their error bars, indicating a local minimum. Table III shows an example of the carbon atom.

However, rather than taking all zeros as an initial guess for variational parameters, if we start from Schmidt and Moskowitz's optimized wave function, a smaller but still sharp decrease occurs at the first iteration. For the atom B, we obtained about 7% more correlation energy in one iteration (see Table IV).

As one can see from Figs. 1–3, the energy derivatives are much smoother than the energy itself. As a result, it is much easier to find the parameter value which gives $dE/dc = 0$ than to locate the minimum from energy data alone. As discussed in Sec. III, the general theorem of the local value derivatives permits reduction of noise associated with the energy derivatives for a much more efficient and reliable wave function optimization in VMC.

After the optimization, the Hessian matrix is diagonal-

TABLE III. An optimization procedure for atom C, with initial parameters as zeros.

Iteration	Energy	Error bar
0	-37.687 45	0.000 39
1	-37.800 80	0.000 13
2	-37.809 45	0.000 12
3	-37.809 01	0.000 11
4	-37.809 18	0.000 11

TABLE IV. An optimization procedure for atom B, with optimized initial values from Ref. 9.

Iteration	Energy	Error bar
0	-24.611 09	0.000 27
1	-24.620 44	0.000 28
2	-24.620 58	0.000 29
3	-24.620 43	0.000 28
4	-24.620 83	0.000 28

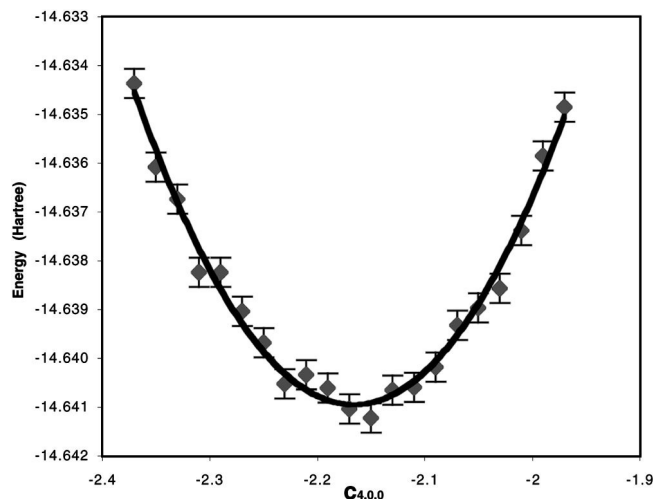


FIG. 1. Energy minimization: energies and error bars for the Be atom, as parameter for $m=4$, $n=0$, $o=0$, is varied.

ized to check the positivity of the eigenvalues. All of the eigenvalues are positive or small negative numbers. A positive definite Hessian guarantees all downhill movement to reach a real local minimum. The negative values are much smaller than their error bars, indicating search directions with tiny positive curvature.

V. CONCLUSIONS

We have explored a new method to optimize wave functions in VMC calculations. This method is a direct application of energy minimization. It is very efficient, giving quadratic convergence, and it is straightforwardly applicable to systems having a large number of parameters. In direct comparisons using identical trial wave functions, the current

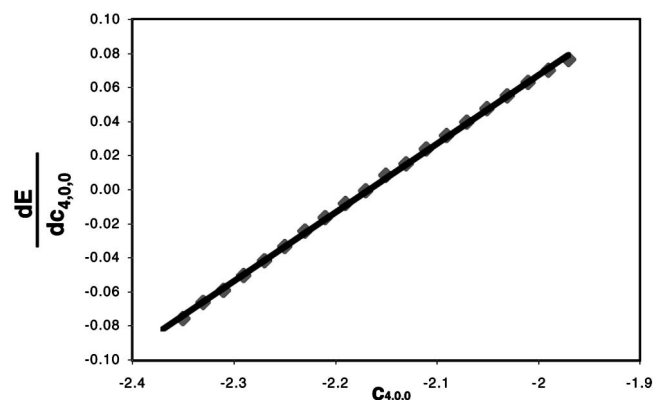


FIG. 2. Energy minimization: first derivative of the energy with respect to the same parameter as Fig. 1.

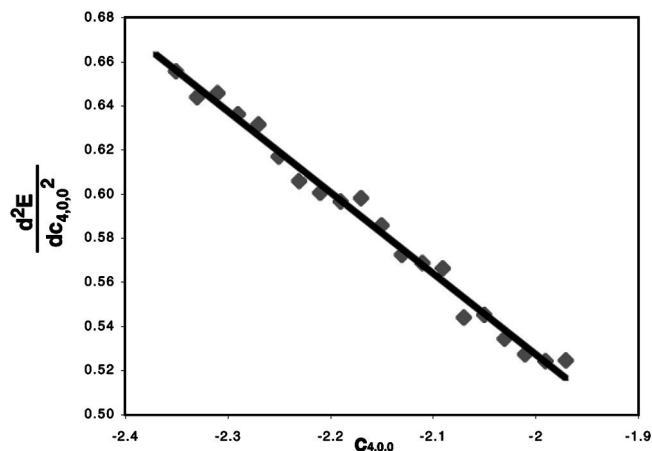


FIG. 3. Energy minimization: second derivative of the energy with respect to the same parameter as Fig. 1.

method yields significantly lower energy expectation values than are achieved with variance minimization for all first-row atoms.

ACKNOWLEDGMENTS

This work was supported by NSF Grant DMR 97-02514. A.M.R. acknowledges support of the Alfred P. Sloan Foundation and the Laboratory for Research on the Structure of Matter at the University of Pennsylvania. Computational support was provided by the San Diego Supercomputer Center and the National Center for Supercomputing Applications.

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