

**RESERVE THIS SPACE**

## **Electronic Quantum Monte Carlo Calculations of Energies and Atomic Forces for Diatomic and Polyatomic Molecules**

**Myung Won Lee<sup>1</sup>, Massimo Mella<sup>2</sup>, and Andrew M. Rappe<sup>1,\*</sup>**

<sup>1</sup> **The Makineni Theoretical Laboratories  
Department of Chemistry, University of Pennsylvania,  
Philadelphia, Pennsylvania 19104-6323**

<sup>2</sup> **School of Chemistry, Cardiff University,  
P.O. Box 912, Cardiff CF10 3TB, United Kingdom**

We calculated the energies and atomic forces of first-row monohydrides, carbon monoxide, and small organic polyatomic molecules using quantum Monte Carlo (QMC) method. Accurate forces were obtained with the method of Casalegno, Mella, and Rappe, combining the Hellmann-Feynman theorem forces calculated by the Assaraf-Caffarel method with a many-body Pulay correction. Improved algorithms for the minimization of the variational integral were useful in the force calculations.

**RESERVE THIS SPACE**

## Introduction

While quantum Monte Carlo (QMC) has become quite successful in computing ground-state total energies, the calculation of properties other than energies has been less favorable. The accurate QMC calculation of atomic forces has been enabled through the recent developments by Assaraf and Caffarel (1,2), Filippi and Umrigar (3), Casalegno *et al.* (4), Chiesa *et al.* (5), and others.

The atomic force calculation can be extended to more complex systems(ZZZ cite Lee2005 here too!ZZZ), and we applied this method to all the first-row monohydrides, carbon monoxide, and small organic polyatomic molecules such as the methylene radical, methyl radical, methane, and benzene. The first and second derivatives of the variational energy were analytically computed, and used to perform Newton's method parameter updates (6). For more efficient calculation of energies and forces, improved methods for optimizing variational Monte Carlo (VMC) wave functions were used (7). In general, the direct application of the variational principle yields significantly lower energy than variance minimization methods, so minimizing the energy is advantageous. The wave functions optimized in VMC were used as a guiding function in diffusion Monte Carlo (DMC) to compute more accurate energies.

Dissociation energies could be obtained from the total energy calculation of diatomic and polyatomic molecules. The computed results agree well with experiment. The dissociation energies from our VMC calculations give better results than the values obtained through the variance minimization technique reported in Ref. (8).

## Theoretical Background

The trial wave function we used is the product of Slater determinants of up-spin and down-spin electrons and a correlation factor containing the variational parameters:  $\psi_T = D^\uparrow D^\downarrow \exp(U)$

where

ZZZ Am I right that you need sum over alpha, and are my variables more right than yours? Delete one. ZZZ

$$U = \sum_{\alpha} \sum_i \sum_{j>i} \sum_k c_{k\alpha} \left( \bar{r}_{i\alpha}^{m_k} \bar{r}_{j\alpha}^{n_k} + \bar{r}_{j\alpha}^{m_k} \bar{r}_{i\alpha}^{n_k} \right) \bar{r}_{ij}^{o_k}$$

$$U = \sum_i \sum_{j>i} \sum_k c_k \left( r_{i\alpha_k}^{m_k} r_{j\alpha_k}^{n_k} + r_{j\alpha_k}^{m_k} r_{i\alpha_k}^{n_k} \right) r_{ij}^{o_k} \quad \text{and} \quad \bar{r}_{ij} = br_{ij} / (1 + br_{ij}) \quad \text{with } b = 1 \text{ inverse Bohr.}$$

Newton's method was used in optimizing the parameters in the trial function in VMC. To improve the stability of the algorithm, we used the singular value decomposition (SVD). In addition, we used the steepest descent method in the initial stage of calculation and to the directions discarded in the SVD method for some calculations as described in Ref. (7).

Atomic forces can be calculated by taking the first derivative of energy with respect to the nuclear coordinates:

$$\langle F_{q\alpha} \rangle = - \frac{\partial}{\partial R_{q\alpha}} \frac{\langle \psi_T | H | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle}$$

where  $q$  represents  $x, y,$  or  $z$  coordinate,  $\alpha$  is a nucleus index, and  $R_{q\alpha}$  is nuclear coordinates. For energy minimized trial wave functions, it can be shown that the force is given by  $\langle F_{q\alpha} \rangle = \langle F_{q\alpha}^{\text{HFT}} \rangle + \langle F_{q\alpha}^{\text{Pulay}} \rangle$  as described in Ref. (4).

For VMC,  $\langle F_{q\alpha}^{\text{HFT}} \rangle$  can be calculated efficiently by using the following expression, which is a generalized form of the equation proposed by Assaraf and Caffarel (1):

$$\langle F_{q\alpha}^{\text{HFT}} \rangle = \langle F_{q\alpha}^{\text{AC}} \rangle = Z_{\alpha} \sum_{I \neq \alpha} Z_I \frac{(R_{q\alpha} - R_{qI})}{|\mathbf{R}_I - \mathbf{R}_{\alpha}|^3} - \sum_{I=1}^{N_{\text{elec}}} \nabla_I Q_{q\alpha} \cdot \frac{\nabla_I \psi_T}{\psi_T}$$

where  $Q_{q\alpha} = -Z_{\alpha} \sum_{I=1}^{N_{\text{elec}}} (r_{qi} - R_{q\alpha}) / |\mathbf{r}_i - \mathbf{R}_{\alpha}|$  and this term differs for each component. Similar expression can be used in the DMC case. Pulay correction term for VMC is given by

$$\langle F_{q\alpha}^{\text{Pulay}} \rangle = -2 \frac{\langle \partial \psi_T / \partial R_{q\alpha} | H | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle} + 2 \langle E_L \rangle \frac{\langle \partial \psi_T / \partial R_{q\alpha} | \psi_T \rangle}{\langle \psi_T | \psi_T \rangle}$$

$$= -2 \left\langle \frac{\partial \psi_T}{\partial R_{q\alpha}} \frac{E_L}{\psi_T} \right\rangle + 2 \langle E_L \rangle \left\langle \frac{\partial \psi_T}{\partial R_{q\alpha}} \frac{1}{\psi_T} \right\rangle$$

and similar equation can be used for DMC (4).

## Results and Discussion

We calculated the energies and forces of first-row monohydrides and carbon monoxide at 5 different bond distances around the experimental bond length (0.90, 0.95, 1.00, 1.05, and 1.10  $r_{\text{exp}}$ ). We fitted the result to the Morse potential to take the anharmonicity into consideration.

Since the number of data points is small, we used the energy and force results simultaneously in the fitting to the Morse potential to get better result. By this fitting, various properties of diatomic molecules, such as equilibrium bond lengths, harmonic vibrational frequencies, and anharmonicity constants could be obtained (7).

Dissociation energies could also be calculated for these diatomic molecules by taking the differences between the energies of molecules and the energies of atoms. The dissociation energies obtained from our VMC and DMC calculation and Hartree-Fock calculation are summarized in Table I, together with VMC and DMC values and experimental values from Ref. (8). Our VMC dissociation energies are closer to the experimental values than those given by L•chow and Anderson (8), while our DMC results are similar to theirs. We think that better VMC results in our calculation can be attributed to the energy minimization method, as compared to the variance minimization method used in Ref. (8).

**Table I. Dissociation energies of diatomic molecules in kcal/mol**

	H-F	VMC	DMC	VMC <sup>a</sup>	DMC <sup>a</sup>	Exp <sup>a</sup>
LiH	34.2	54.7	57.8	45.7	57.8	58.0
BeH	50.3	57.9	55.7	49.4	52.1	49.8
BH	64.2	82.7	84.7	63	84.8	84.1
CH	56.9	81.1	83.5	81	83.9	83.9
NH	48.1	80.2	82.3	77	81.4	80.5-84.7
OH	68.6	105.1	106.4	86	106.4	106.6
HF	98.8	140.4	141.4	130	141.3	141.5

<sup>a</sup> from Ref. (8)

The following compares the force components for LiH molecule at the bond distance of  $0.9 r_{\text{exp}}$ . First, the force on hydrogen atom is displayed in Figure 1 (a) and (b). As can be seen in the figure, Assaraf-Caffarel method reduces the noise considerably, enabling the efficient calculation of Hellmann-Feynman theorem force. In the case of the force on hydrogen atom, Pulay correction was close to zero, so that the total force was quite similar to Assaraf-Caffarel force, as can be seen in Figure 1 (b).

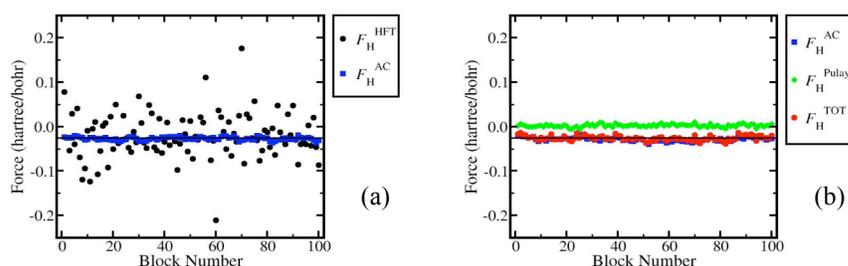


Figure 1. Force on hydrogen atom in the VMC force calculation of LiH molecule. (a) Hellmann-Feynman theorem force and Assaraf-Caffarel force, and (b) Assaraf-Caffarel force, Pulay correction, and total force.

We also calculated the force on Li atom, which should be the negative of the force on hydrogen atom, as LiH is a diatomic molecule, and it is shown in Figure 2 (a) and (b). The black horizontal line in the figure denotes the negative of the force on hydrogen atom.

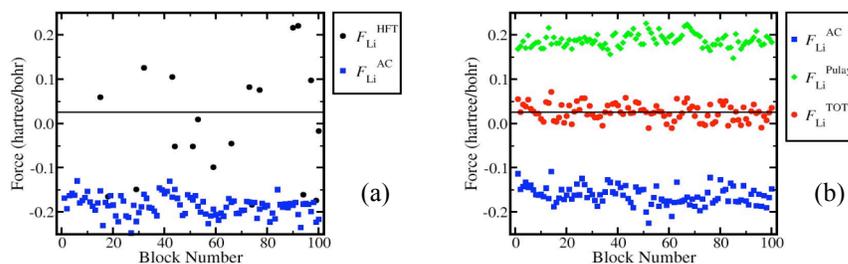


Figure 2. Force on lithium atom in the VMC force calculation of LiH molecule. (a) Hellmann-Feynman theorem force and Assaraf-Caffarel force, and (b) Assaraf-Caffarel force, Pulay correction, and total force.

In the case of the force on lithium atom, however, although Assaraf-Caffarel method reduces the noise in the Hellmann-Feynman theorem force calculation, Assaraf-Caffarel force does not agree with the negative of the force on hydrogen atom. The total force on lithium atom obtained by adding Assaraf-Caffarel force and Pulay correction agrees well with the negative of the force on hydrogen atom, as can be clearly seen in Figure 2 (b).

For other hydrides, we calculated the atomic force only on hydrogen atom. For all cases, Pulay correction was very small. For carbon monoxide, however, the magnitude of Pulay correction was larger than that of Assaraf-Caffarel force, and was important in the obtaining of correct atomic forces. As can be seen in Figure 3, the total force on carbon atom is similar to the total force on oxygen atom in magnitude, and their directions are opposite, while for Assaraf-Caffarel force, their magnitudes for carbon atom and oxygen atom are quite different. It seems that Pulay correction is indispensable in the calculation of forces on nonhydrogen atoms.

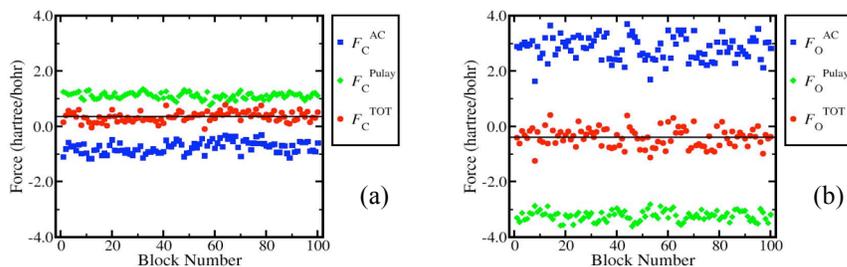


Figure 3. Force calculation of CO molecule. (a) Force on carbon atom, and (b) force on oxygen atom.

We performed VMC and DMC calculation of energies for methylene radical, methyl radical, and methane molecule at their experimental geometries and then obtained the dissociation energies. The result is summarized in Table II together with Hartree-Fock result. Hartree-Fock method shows poor result, as is the case for the dissociation energies of diatomic molecules, while QMC method considerably corrects errors in the Hartree-Fock calculation, making it promising as an accurate method for the calculation of reaction energies. It can

be noted that QMC method is good in predicting the bond dissociation energies irrespective of the spin states of the reactant and product molecules.

**Table II. Dissociation energies of some polyatomic molecules in kcal/mol**

Process	H-F	VMC	DMC	Exp
$\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$	88	109	112	104
$\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})$	99	122	125	108
$\text{CH}_2(\text{g}) \rightarrow \text{CH}(\text{g}) + \text{H}(\text{g})$	86	101	103	102

For  $\text{CH}_2$  molecule, we calculated forces on each atom at various geometries, and the calculated forces were in the direction to restore the experimental geometry, as is the case for LiH molecule above. The force on each atom is depicted in Figure 4 using an arrow on each atom, whose direction is the same as the direction of the force and the magnitude proportional to the magnitude of the force. At experimental geometry, each force component was close to zero as expected. For other geometries where the bond lengths or bond angle are changed, the forces we obtained were generally as expected. While the forces on hydrogen atoms look correct in all cases, the force on carbon atom deviated from the expected directions in some cases. We could calculate the forces on hydrogen atoms quite accurately, but we think that we need more calculation time for more accurate forces on larger atoms.

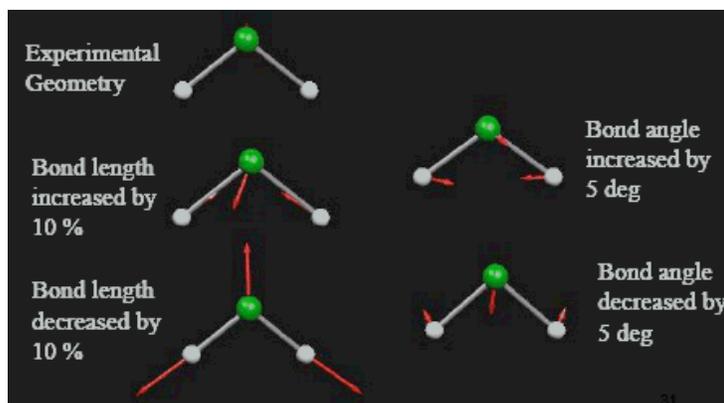


Figure 4. Force calculation of methylene radical at various geometries

The preliminary result of benzene QMC energy calculation at experimental geometry is shown in Figure 5. The first data point at about -230.8 hartree is the reproduction of Hartree-Fock energy. Initially, the steepest descent method was applied (iterations 2-17). We used 4 parameters for iterations 2-6, 40 parameters for iterations 7-10, and 64 parameters for iterations 11-17. Even after these steepest descent steps, the noise in the Hessian was too large that it was difficult to apply Newton's method when we used the equation for the Hessian calculation in our previous work (6). So we used the Hessian in covariance form as proposed by Umrigar and Filippi (9):

$$\begin{aligned} \bar{E}_{ij} = 2 & \left[ \left\langle \left( \frac{\psi_{ij}}{\psi} + \frac{\psi_i \psi_j}{\psi^2} \right) (E_L - \bar{E}) \right\rangle - \left\langle \frac{\psi_i}{\psi} \right\rangle \bar{E}_j - \left\langle \frac{\psi_j}{\psi} \right\rangle \bar{E}_i \right] \\ & + \left\langle \frac{\psi_i}{\psi} E_{L,j} \right\rangle - \left\langle \frac{\psi_i}{\psi} \right\rangle \langle E_{L,j} \rangle + \left\langle \frac{\psi_j}{\psi} E_{L,i} \right\rangle - \left\langle \frac{\psi_j}{\psi} \right\rangle \langle E_{L,i} \rangle. \end{aligned}$$

This scheme reduced the noise considerably and we could apply Newton's method as used for diatomic molecules. After VMC calculation, we performed DMC calculation (iterations 23-26), which reduced the energy even more.

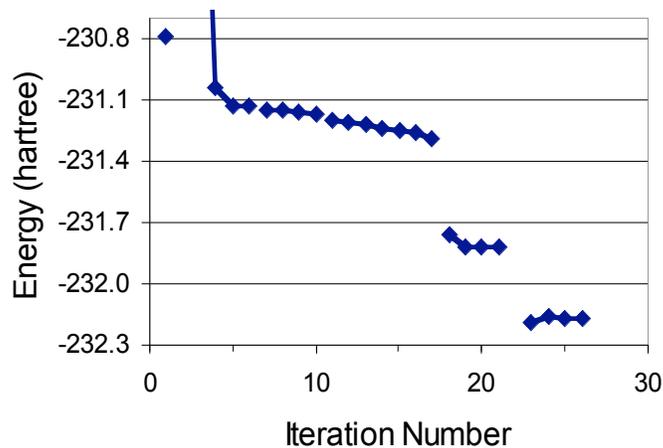


Figure 5. Energy of benzene in the course of QMC calculation

## Conclusions

The force calculation method combining energy minimization, a renormalized Hellmann-Feynman estimator, and Pulay correction worked well with all the first-row hydride molecules, carbon monoxide, and some polyatomic molecules with small extra effort.

The energy minimization method in VMC is useful, but it requires an effective optimization scheme. The addition of steepest descents to the initial steps and to the subspace neglected by Newton's method with SVD seems to be advantageous for the molecular systems we investigated. For larger systems, the use of covariance form in the Hessian calculation seems indispensable due to the large noise.

We could calculate accurate harmonic vibrational frequencies and anharmonicity constants of diatomic molecules by fitting QMC results to the Morse potential, achieving good agreement between QMC calculations and experiment for these vibrational parameters.

## Acknowledgments

This work was supported by the Air Force Office of Scientific Research, Air Force Material Command, USAF, under Grant No. FA9550-04-1-0077. Computational support was provided by the Defense University Research Instrumentation Program, and by the NSF CRIF program, Grant CHE-0131132.

## References

1. Assaraf, R.; Caffarel, M. *J. Chem. Phys.* **2000**, *113*, 4028
2. Assaraf, R.; Caffarel, M. *J. Chem. Phys.* **2003**, *119*, 10536
3. Filippi, C.; Umrigar, C. *J. Phys. Rev. B* **2000**, *61*, R16291
4. Casalegno, M.; Mella, M.; Rappe, A. M. *J. Chem. Phys.* **2003**, *118*, 7193
5. Chiesa, S.; Ceperley, D. M.; Zhang, S. *Phys. Rev. Lett.* **2005**, *94*, 036404
6. Lin, X.; Zhang, H.; Rappe, A. M. *J. Chem. Phys.* **2000**, *112*, 2650
7. Lee, M. W.; Mella, M.; Rappe, A. M. *J. Chem. Phys.* **2005**, *122*, 244103.
8. L'chou A.; Anderson, J. B. *J. Chem. Phys.* **1996**, *105*, 7573
9. Umrigar, C. J.; Filippi, C. *Phys. Rev. Lett.* **2005**, *94*, 150201