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Force calculation of polyatomic molecules in quantum Monte Carlo using Pulay's corrections

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We calculated the variational and diffusion quantum Monte Carlo forces using the Hellmann–Feynman theorem and Pulay's correction for the first-row diatomic and triatomic molecules (CO, NO, CO₂ and NO₂). It is demonstrated that Pulay's correction is important for accurate calculation of forces on non-hydrogen atoms.

Keywords: Quantum Monte Carlo; Variational Monte Carlo; Diffusion Monte Carlo; Pulay's correction; Force calculation

1. Introduction

Quantum Monte Carlo (QMC) methods have been demonstrated to be a powerful tool for computing ground state total energies of atomic, molecular and solid systems [1–3]. The development of QMC methods for electronic structure calculations is driven by the possibility to achieve high accuracy at a reasonable computational cost. In recent years, two flavours of QMC, variational (VMC) and diffusion (DMC), received much attention as quantum chemistry tools due to their conceptual simplicity. In VMC, a parameterized form of a many-electron wave function is chosen, and the total energy is optimized with respect to the parameters using Monte Carlo techniques. In DMC, the Schrödinger equation is interpreted as a diffusion equation. These two methods are often used in tandem. Namely, VMC is used first, and then, DMC is used with the VMC wave function, which substantially improves the convergence of DMC and removes the limitations posed by the particular choice of the wave function form in VMC. Due to the good trade-off between the accuracy and computational cost, accurate calculations of total energies of relatively large molecular systems have been successfully performed [4–6].

Although similar high quality trade-off should be expected in QMC calculations of properties other than total energy (e.g. forces and polarizabilities), in practice the techniques used to calculate energy in QMC cannot be directly applied to other properties due to a much slower convergence. The reason for this difference originates from the so-called zero-variance property of the energy: in the limit of an exact trial wave function, the statistical error in energy estimate becomes zero, which is not in general true for other observables [7, 8]. Moreover, in the case of force, the variance integral is not only finite, it diverges [8].

The atomic force calculations within the QMC formalism became feasible only recently [8–12]. An important step has been made by Assaraf and Caffarel [8], who introduced a renormalized force operator, which has a finite (although non-zero) variance. Based on these crucial advances, the next important step towards accurate force calculations was made by our group [10, 13]. All previous work focused on the Hellmann–Feynman contribution to force, and no attention was devoted to Pulay’s correction [14]. If the exact wave function is given, the application of the Hellmann–Feynman theorem will give the exact force on each atom. In VMC, Pulay’s correction appears due to the approximate form of the wave function. In DMC, Pulay’s correction is associated with the mixed probability density.

Very recently, Chiesa et al. [12] suggested a different way of modifying the force estimator to insure finite variance. They demonstrated the feasibility of their approach by calculating very accurate optimized geometries of small diatomic and polyatomic molecules with one first-row atom, as well as harmonic frequencies of hydrogen-containing diatomics. However, as they did...
not include Pulay’s correction in their VMC calculation for the LiH molecule, for example, the forces on Li and H atoms differed in magnitude.

In this paper, we demonstrate the importance of Pulay’s correction for both VMC and DMC by computing the forces in diatomic and triatomic molecules composed of first-row atoms (CO, NO, CO₂ and NO₂). Our results suggest that the magnitude of this correction is comparable to that of the Hellmann–Feynman theorem force for the molecules with first-row atoms.

2. Theory

The trial wave function we use is the product of Slater determinants of up-spin (\(D^+\)) and down-spin (\(D^-\)) electrons, and a Jastrow correlation factor in Schmidt and Moskowitz form [15] first introduced by Boys and Handy [16], with variational parameters (\(c_{\alpha\beta}\))

\[
\Psi_T = D^+ D^- \exp \left( \sum_{\alpha} \sum_{i} \sum_{j<i} U_{\alpha ij} \right),
\]

\[
U_{\alpha ij} = \sum_k c_{\alpha\beta} \left( \bar{r} \delta_{i\alpha} \bar{r}^*_{\beta j} + \bar{r} \delta_{i\beta} \bar{r}^*_{\alpha j} \right),
\]

where \( \bar{r} = br/(1 + br) \) with \( b = 1 \) bohr\(^{-1}\), and \( m_{\alpha\beta} \), \( n_{\alpha\beta} \) and \( o_{\alpha\beta} \) are integers.

Newton’s method is used to minimize the energy of the VMC trial wave function, \( \tilde{E}_q = \langle \Psi_T | \hat{H} | \Psi_T \rangle \). To improve the stability of the algorithm, we use the singular value decomposition (SVD). We employ the steepest descent method for the directions discarded in the SVD method [13].

To decrease the noise in the Hessian calculation, we use the expression for the Hessian in symmetrized covariance form as proposed by Umrigar in Hessian and Filippi [6],

\[
\tilde{E}_q = 2 \left( \langle \Psi_I | \hat{H} | \Psi_T \rangle \right) (E_L - \tilde{E}) - 2 \left( \langle \Psi_I | \hat{H} | \Psi_T \rangle \right) \tilde{E}_j - 2 \left( \langle \Psi_I | \hat{H} | \Psi_T \rangle \right) \tilde{E}_i + \left( \langle \Psi_I | \hat{H} | \Psi_T \rangle \right) (E_L - \tilde{E})
\]

where the subscript \( i \) (or \( j \)) means the partial derivative with respect to the \( i \)th (or \( j \)th) variational parameter.

Atomic forces are the first total derivative of the energy with respect to the nuclear coordinates, and in the case of VMC, it is given by

\[
F_{aq} = - \frac{d}{dR_{aq}} \frac{\langle \Psi_T | \hat{H} | \Psi_T \rangle}{\langle \Psi_T | \Psi_T \rangle},
\]

where \( \alpha \) indexes the nuclei, \( q \) represents the \( x \), \( y \) or \( z \) component and \( R_{aq} \) is a nuclear coordinate. The total derivative can be represented as the sum of the following two distinct terms; (i) the Hellmann–Feynman theorem term and (ii) Pulay’s correction. Pulay’s correction can be further decomposed into a contribution due to the explicit dependence of the wave function on atomic coordinates and a contribution due to the change of the wave function parameters upon atomic displacements. The second contribution is zero if the parameters are obtained variationally [17]. Since energy minimized trial wave functions are used in this work, the second contribution is zero, and the force is given by [10]

\[
(F_{aq}) = (F_{aq}^{\text{HFT}}) + (F_{aq}^{\text{Pulay}}),
\]

where HFT denotes the Hellmann–Feynman theorem term, and Pulay’s correction \( (F_{aq}^{\text{Pulay}}) \) contains only a contribution due to the explicit dependence of the trial wave function on atomic coordinates.

To eliminate the problems associated with the infinite variance of the Hellmann–Feynman estimator \( (F_{aq}^{\text{HFT}}) \), we adopt the renormalization approach proposed by Assaraf and Caffarel [8] and extend it to polyatomic molecules.

\[
(F_{aq}^{\text{HFT}}) = (F_{aq}^{\text{AC}})_{\text{VMC}} = Z_a \sum_{i \neq a} Z_i \frac{R_{aq} - R_{iq}}{|R_i - R_a|^3} - \sum_{i} \nabla Q_{aq} \frac{\nabla \Psi_T}{\Psi_T},
\]

with \( Q_{aq} = -Z_a \sum_{i} (r_{aq} - R_{aq})/|r_i - R_a| \) being different for each component. For DMC, the following expression is used:

\[
(F_{aq}^{\text{HFT}})_{\text{DMC}} = (F_{aq}^{\text{AC}})_{\text{DMC}} = Z_a \sum_{i \neq a} Z_i \frac{R_{aq} - R_{iq}}{|R_i - R_a|^3} - \sum_{i} \nabla Q_{aq} \frac{\nabla \Psi_T}{\Psi_T} + (E_L Q_{aq}) - (E_L)Q_{aq}.
\]

Pulay’s correction for VMC is given by

\[
(F_{aq}^{\text{Pulay}})_{\text{VMC}} = -2 \left( \frac{\partial \Psi_T}{\partial R_{aq}} |\tilde{E}_L\rangle + 2 \langle \tilde{E}_L | \frac{\partial \Psi_T}{\partial R_{aq}} \frac{1}{\Psi_T} \right),
\]
and for DMC
\[
\langle F_{p_{\text{Pulay}}} \rangle_{\text{DMC}} = -\left(\frac{\partial \Psi}{\partial R_{aq}} \frac{E_L}{\Psi} + \frac{\partial \Psi}{\partial R_{aq}} \frac{1}{E_L} \right),
\]
as described in [10].

3. Computational

We compute the VMC and DMC forces for carbon monoxide (CO), nitric oxide (NO), carbon dioxide (CO₂) and nitrogen dioxide (NO₂) at several distorted geometries around the experimental equilibrium geometry for each molecule. The quality of the computed forces is tested by comparison with the forces obtained by direct differentiation of the Morse fit to the energy for both VMC and DMC. The energies and forces are calculated at five different bond lengths: 0.90, 0.95, 1.00, 1.05 and 1.10 times \(r_{\text{exp}}\), where \(r_{\text{exp}}\) is the corresponding experimental equilibrium bond length. For NO₂ and CO₂, the potential energy curve and the forces are also calculated at a few different bond angles, with the N–O and C–O bond lengths being fixed at corresponding \(r_{\text{exp}}\)'s.

For all calculations, the Slater-type orbital (STO) basis set is used (see [13] for details). The Slater determinants in the trial wave function in equation (1) are obtained from Hartree–Fock calculations using quantum chemistry package GAMESS [18]. To use STOs in GAMESS, we expressed each STO as a linear combination of 6–10 Gaussians. Only the \(c_{ka}\) parameters in the Jastrow factor are varied in the optimization process. The Hessian is calculated by the scheme proposed by Umrigar and Filippi [6]. For diatomic molecules, 30 parameters are used, and for triatomic molecules, 43 parameters are used. The optimized trial wave function in VMC is used as a guiding function in DMC. Since a small number of persistent configurations may have a large influence on the energy or force, walkers that do not move for 10–20 consecutive steps have been replaced by copies of randomly chosen walkers.

4. Results and discussion

The calculated total energies and forces for CO and NO are shown in figures 1(a) and (b). The slopes of the black line segments in these graphs correspond to the calculated forces.

To make sure that the sum of forces on all atoms is zero within statistical error, and to illustrate the generality of the method, we calculate the \(x\), \(y\) and \(z\) components of the forces for each atom in the molecules. As an example, we summarize the results for CO in table 1. The C atom is placed at the origin, and the O atom is on the positive \(x\) axis at 0.95 \(r_{\text{exp}}\). It can be seen that the total forces perpendicular to the molecular axis deviate from zero by \(\sim 0.02\) hartree bohr\(^{-1}\) at most, while the sum of the \(x\) component of the total forces on both atoms is different from zero by \(\sim 0.006\) hartree bohr\(^{-1}\). Similar results have been obtained with DMC. In all cases, these forces will continue to approach zero with more extensive stochastic sampling.

In our previous work [13], Pulay’s correction to the forces on hydrogen atoms was negligibly small compared to the HFT force value, similar in magnitude to the HFT error bar. However, the results in table 1 clearly demonstrate that Pulay’s correction is indispen-

![Figure 1](image-url)
Table 1. Calculated VMC force components of CO at bond distance 0.95$r_{\text{exp}}$. Error bars are shown in parentheses.

<table>
<thead>
<tr>
<th>Bond distance (r$_{\text{exp}}$)</th>
<th>$F_{\text{VMC}}^C$</th>
<th>$F_{\text{Morse}}^C$</th>
<th>$F_{\text{DMC}}^C$</th>
<th>$F_{\text{Morse}}^C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>-0.367 (6)</td>
<td>-0.357 (11)</td>
<td>-0.394 (7)</td>
<td>-0.389 (12)</td>
</tr>
<tr>
<td>0.95</td>
<td>-0.139 (5)</td>
<td>-0.135 (2)</td>
<td>-0.140 (7)</td>
<td>-0.146 (3)</td>
</tr>
<tr>
<td>1.00</td>
<td>0.028 (5)</td>
<td>0.025 (3)</td>
<td>0.016 (8)</td>
<td>0.017 (4)</td>
</tr>
<tr>
<td>1.05</td>
<td>0.122 (7)</td>
<td>0.136 (2)</td>
<td>0.138 (8)</td>
<td>0.122 (3)</td>
</tr>
<tr>
<td>1.10</td>
<td>0.203 (6)</td>
<td>0.210 (7)</td>
<td>0.197 (7)</td>
<td>0.187 (8)</td>
</tr>
</tbody>
</table>

Table 2. $x$ component of VMC and DMC total force of CO obtained by combining HFT and Pulay’s correction and the force computed from the slope of the Morse potential fit of the energy.

<table>
<thead>
<tr>
<th>Bond distance (r$_{\text{exp}}$)</th>
<th>$F_{\text{VMC}}^x$</th>
<th>$F_{\text{Morse}}^x$</th>
<th>$F_{\text{DMC}}^x$</th>
<th>$F_{\text{Morse}}^x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>-0.189 (7)</td>
<td>0.198 (8)</td>
<td>0.178 (8)</td>
<td>0.166 (8)</td>
</tr>
<tr>
<td>0.95</td>
<td>-0.114 (7)</td>
<td>0.141 (2)</td>
<td>0.113 (9)</td>
<td>0.120 (3)</td>
</tr>
<tr>
<td>1.00</td>
<td>0.036 (7)</td>
<td>0.047 (3)</td>
<td>0.036 (9)</td>
<td>0.033 (4)</td>
</tr>
<tr>
<td>1.05</td>
<td>0.114 (7)</td>
<td>0.141 (2)</td>
<td>0.113 (9)</td>
<td>0.120 (3)</td>
</tr>
<tr>
<td>1.10</td>
<td>0.189 (7)</td>
<td>0.198 (8)</td>
<td>0.178 (8)</td>
<td>0.166 (8)</td>
</tr>
</tbody>
</table>

Figure 2. Calculated forces for the CO$_2$ molecule at several geometries. (a) Experimental geometry, (b) bond lengths increased by 10%, and (c) bond lengths decreased by 10%.

Table 3. $x$ component of VMC and DMC total force of NO obtained by combining HFT and Pulay’s correction and the force computed from the slope of the Morse potential fit of the energy.

<table>
<thead>
<tr>
<th>Bond distance (r$_{\text{exp}}$)</th>
<th>$F_{\text{VMC}}^x$</th>
<th>$F_{\text{Morse}}^x$</th>
<th>$F_{\text{DMC}}^x$</th>
<th>$F_{\text{Morse}}^x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.90</td>
<td>-0.316 (7)</td>
<td>-0.315 (11)</td>
<td>-0.322 (8)</td>
<td>-0.355 (14)</td>
</tr>
<tr>
<td>0.95</td>
<td>-0.100 (7)</td>
<td>-0.099 (3)</td>
<td>-0.103 (7)</td>
<td>-0.115 (3)</td>
</tr>
<tr>
<td>1.00</td>
<td>0.038 (7)</td>
<td>0.047 (3)</td>
<td>0.036 (9)</td>
<td>0.033 (4)</td>
</tr>
<tr>
<td>1.05</td>
<td>0.114 (7)</td>
<td>0.141 (2)</td>
<td>0.113 (9)</td>
<td>0.120 (3)</td>
</tr>
<tr>
<td>1.10</td>
<td>0.189 (7)</td>
<td>0.198 (8)</td>
<td>0.178 (8)</td>
<td>0.166 (8)</td>
</tr>
</tbody>
</table>

The choice of the Morse potential to fit the energy is quite important for molecules containing any atoms heavier than hydrogen. The calculations provide further proof that combining efficient energy minimization, a renormalized Hellmann–Feynman estimator, and Pulay’s correction, results in an accurate and affordable

5. Conclusions

Our results demonstrate that Pulay’s correction is very important for molecules containing any atoms heavier than hydrogen. The calculations provide further proof that combining efficient energy minimization, a renormalized Hellmann–Feynman estimator, and Pulay’s correction, results in an accurate and affordable
technique for computing forces in QMC. The practical implementation of this technique benefits from using energy minimized VMC trial wave functions. The use of the symmetrized covariance form of the Hessian proves to be very useful for reducing the stochastic noise and making the energy minimization more efficient.

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