

A quantum Monte Carlo and density functional theory study of the electronic structure of peroxy nitrite anion

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Single point calculations of the ground state electronic structure of peroxy nitrite anion have been performed at the optimized *cis* geometry using the restricted Hartree–Fock (RHF), Møller Plesset second order perturbation theory (MP2), generalized gradient approximation density functional theory (GGA DFT) in the B3LYP form and two quantum Monte Carlo (QMC) methods, variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC). These calculations reveal differences in atomization energies estimated by B3LYP (287.03 kcal/mol), MP2 (290.84 kcal/mol), and DMC, 307.4(1.9) kcal/mol, as compared to experiment, 313(1) kcal/mol. The error associated with MP2 and B3LYP methods is attributed largely to differential recovery of correlation energies for neutral nitrogen and oxygen atoms relative to the oxygen and peroxy nitrite anions. In addition, basis set studies were carried out to determine potential sources of error in MP2 and B3LYP valence energy values. Our studies indicate that MP2 and B3LYP valence energies are strongly dependent on the presence of diffuse functions for the negative ions O^- and $ONOO^-$. © 2003 American Institute of Physics. [DOI: 10.1063/1.1544732]

I. INTRODUCTION

Peroxy nitrite ($ONOO^-$) is formed by the direct and rapid reaction of nitric oxide with superoxide anion.^{1–3} Because $ONOO^-$ can act as a one-electron oxidant or a two-electron oxidant, it is able to react with a number of biomolecules including proteins,^{4–11} DNA,^{12,13} lipids,¹⁴ and antioxidants.^{15,16} The reactivity profile of peroxy nitrite suggests that it is capable of crossing biological membranes faster than its known decomposition rate.¹⁷ Studies also suggest that production of peroxy nitrite plays a pivotal role in the apoptosis (programmed cell death) of neural cells¹⁸ and aortic smooth muscle cells in rats.¹⁹ Similarly, peroxy nitrite has been shown to induce apoptosis in human leukemia cells^{20,21} with clear dependence on its length of exposure and concentration. The same study also suggested the ineffectiveness of peroxy nitrite at inducing apoptosis in some normal endothelial human cells.²⁰ The high reactivity of peroxy nitrite and its potential role in a wide variety of human diseases have stimulated our present study.

Theoretical studies of peroxy nitrite^{22–25} have given some insight on its geometry and electronic structure. Some properties of this anion have also been inferred from studies of $ONOOM$ ($M=Li,Na,K$) (Ref. 26) or decomposition of $ONOOH$.²⁷ None of these studies focus on direct calculations of the molecule as it is formed *in vivo*, in its unattached ionic state. Factors that may account for the limited application of computational methods to this system are difficulties encountered with some basis set *ab initio* methods in treating negative ions of molecules containing nitrogen and oxygen atoms. Motivated by success with quantum Monte Carlo (QMC) in the diffusion Monte Carlo (DMC) approach in treating negative ions^{28–30} and, in particular, accurate determinations of atomization energies of molecular systems,^{31–34} we undertook the present study to characterize more fully this important system of biological interest.

The remainder of the paper is organized as follows: Section II presents a brief discussion of DMC to highlight the basic ideas of the method; Sec. III describes the equilibrium geometry and some aspects of the electronic structure of $ONOO^-$; Sec. IV presents valence and atomization energies obtained with various basis sets and methods; and Secs. V and VI discuss the results with some commentary on potential sources of error.

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II. COMPUTATIONAL METHODS

A. Variational Monte Carlo (VMC)

There is a similarity between the Schrödinger equation in imaginary time ($\tau=it$), written in atomic units,

$$\frac{\partial\Phi}{\partial\tau} = \frac{1}{2}\nabla^2\Phi + V\Phi \quad (1)$$

and a classical diffusion equation with a rate term,

$$\frac{dC}{dt} = D\nabla^2C + kC. \quad (2)$$

In Eq. (1), Φ is a quantum mechanical wave function, and ∇^2 and V are the kinetic and potential energy operators, respectively. In Eq. (2), C is the concentration, D is the diffusion constant, and k is a rate constant. When the quantum mechanical wave function in Eq. (1), serves as a probability density in imaginary time, no real time dynamics can be obtained.^{35–39} Using Φ in this manner is analogous to considering it as a concentration of electrons undergoing rate and diffusion processes.

The conceptually simple variational Monte Carlo (VMC) method^{40–44} uses Monte Carlo integration to evaluate a trial function. Unlike basis set expansion *ab initio* methods which rely on accurate integration of molecular integrals to achieve high accuracy, VMC trial functions may be of any form. In atomic and molecular applications, this trial function is often a product of an independent particle wave function typically computed in one of the following approximations: Hartree–Fock (HF), configuration interaction (CI), or complete active space self-consistent field (CASSCF), and a correlation function that is explicitly dependent on interparticle distances. The probability distribution used in the Monte Carlo integration is taken as the square modulus of the trial function, and in all-electron VMC the energy is an upper bound to the exact energy of the state being evaluated. The form of the estimator used in VMC is

$$\langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\left\langle \Psi \left| \frac{H\Psi}{\Psi} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Psi | E_L | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle E_L \rangle, \quad (3)$$

where E_L is the “local energy,” defined as $H\Psi(\mathbf{B})/\Psi(\mathbf{R})$.

B. Diffusion Monte Carlo

The DMC method is based on stochastic simulation of the Schrödinger equation in imaginary time; the latter may be written,^{45–47}

$$\frac{\partial f}{\partial t} = \frac{1}{2}\nabla(\nabla - F)f - (E_L - E_T)f, \quad (4)$$

where the distribution

$$f \equiv \Psi_T \Phi. \quad (5)$$

Here Ψ_T is a known wave function and Φ is the exact solution, and

$$F \equiv \ln|\Psi_T|^2 \quad (6)$$

is labeled the quantum force. The parameter E_T is an energy offset, and

$$E_L(\mathbf{R}) \equiv \frac{\hat{H}\Psi_T(\mathbf{R})}{\Psi_T(\mathbf{R})} \quad (7)$$

is the local energy, where \mathbf{R} denotes the $3N$ coordinates of the system. We choose Ψ_T as the product of an independent-particle wave function, Ψ_0 , and a correlation function U , i.e.,

$$\Psi_T = \Psi_0 \exp U, \quad (8)$$

where

$$U \equiv U(r_{ij}, r_{i\alpha}, r_{i\beta}). \quad (9)$$

In Eq. (9), the r_{ij} are electron–electron distances, and the $r_{i\alpha}$ and $r_{i\beta}$ are electron–nuclear distances. The parameter E_T is generally chosen to be close to the expected value of the local energy in order to reduce the magnitude of the last term on the r.h.s. of Eq. (4). The function F produces a drift in the simulation that increases sampling in the regions where the wave function is large. The fixed node approximation imposes the nodal structure of Ψ_T on Φ which insures f is non-negative for all \mathbf{R} .

In the present study, the independent particle wave function Ψ_0 is chosen as a restricted Hartree–Fock (RHF) wave function. The correlation function is a Schmidt–Moskowitz⁴⁴ adaptation of the Boys–Handy function,⁴⁸ which includes terms describing two- and three-body interactions. The correlation function parameters were optimized by minimizing the variance of the energy estimate from a Monte Carlo integration.

There are a number of DMC studies that have demonstrated the successful application of this method in conjunction with effective core potentials (ECP-DMC).^{49–54} More specifically, ECP-DMC studies of second row bond energies and electron affinities have been reported which agree well with experiment^{54,55} and have been able to distinguish between alternative experimental analyses.⁵⁶ The DMC method is relatively insensitive to choice of basis set for the independent-particle part of the trial function. With a single-reference wave function, we used a cc-pVTZ basis set⁵⁷ with no F functions for single-point energy calculations. In DMC, effective sampling of the regions of space occupied by core electrons is costly; it is this additional cost that serves as additional motivation for using ECP's. Estimates of computational effort for all-electron QMC for atoms yield^{55–65} dependence, where Z is the atomic number.⁵⁰ The use of ECP's has been found to reduce this dependence to roughly N^3 , where N is the effective atomic number, or stated more directly, the number of electrons to be simulated.⁵⁰ To provide a more concrete and recent example, we turn to Ref. 31. Table VI of this paper compares the CPU and disk storage requirements of LDA, G2 theory, and DMC calculations, as well as the parallelism and scaling. One finds that LDA is at least an order of magnitude less costly than DMC and G2, and that G2 requires roughly three orders of magnitude more disk storage than LDA and DMC. Timing estimates are subject to variances owing to machine configuration and other system-specific features.

TABLE I. Optimized bond lengths (angstroms) and angles (degrees) of ONOO⁻.

	B3LYP 6-311+G*	B3LYP cc-pVTZ	MP2 cc-pVTZ
O1=N1	1.213	1.214	1.234
N1-O2	1.367	1.362	1.336
O2-O3	1.388	1.382	1.358
O1-N1-O2	116.3	116.1	115.4
N1-O2-O3	118.4	118.4	117.9

In addition to the benefits of ECPs in general, there are alternative ECPs that have been recently developed for the oxygen and nitrogen atoms which enhance the efficiency of DMC simulations. These ECPs, which are similar to the soft ECPs of condensed matter physics⁵⁸ and to a soft ECP reported for carbon,⁵⁹ are characterized by the absence of the r^{-2} term common to ECPs in quantum chemistry.^{59,60} DMC simulations using the soft ECP are found to yield a smaller statistical error bar than the Stevens, Basch, and Krauss (SBK) function⁶⁰ for comparable computing time. The soft ECP also yields comparable valence variational Monte carlo (VMC) energies and slightly lower valence DMC energies, compared to the SBK ECP. For these reasons, we carried out DMC calculations only using soft ECPs.

III. GEOMETRY AND VALENCE ELECTRONIC STRUCTURE

The geometry of ONOO⁻ was optimized at the B3LYP/6-311+G*, B3LYP/cc-pVTZ, and MP2/cc-pVTZ levels. The B3LYP parameters obtained with 6-311+G* (92 basis functions) and cc-pVTZ (140 basis functions) were very close and displayed similar trends as those derived from MP2; see Table I. In agreement with previous studies,^{22,23} our optimizations revealed the planar *cis* conformer as the most stable geometry with outer O1=N1, central N1-O2, and outer O2-O3 bonds (Fig. 1).

Figure 2 shows the frontier Kohn-Sham orbitals of ONOO⁻. The HOMO is mainly localized on the terminal oxygen of the superoxide fragment. By contrast, the LUMO is mainly localized on the nitric oxide fragment and in this regard is analogous to the π^* orbitals of free NO.⁶¹ To check the nature of the singlet ground state of ONOO⁻ both restricted and unrestricted density functional calculations were carried out. The frontier orbitals with α and β spin index were indistinguishable in the unrestricted calculation con-

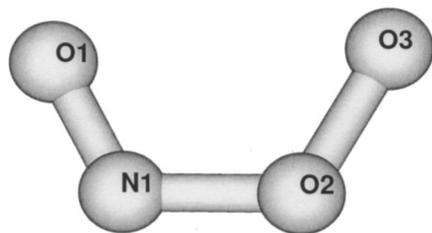


FIG. 1. Optimized geometry of peroxynitrite ion. Metric parameters are given in Table I.

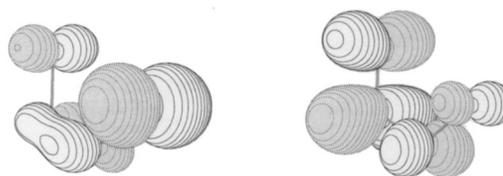


FIG. 2. HOMO (left) and LUMO (right) of peroxynitrite calculated at the B3LYP/cc-pVTZ level. The HOMO is mainly localized on the superoxide fragment, whereas the LUMO is mainly localized on the nitric oxide fragment.

firming the closed-shell singlet character of the ONOO⁻ ground state. We also notice that, despite the auxiliary character of Kohn-Sham orbitals,⁶² which makes it difficult to give them a well defined physical meaning, DFT and *ab initio* wave function methods (MP2) yielded similar trends in frontier orbital composition and charge distribution. As shown in Table II, most of the negative charge is localized on the terminal oxygen of the superoxide fragment (O3), consistent with the spatial distribution of the HOMO. The peroxynitrite anion is known to react with transition metal-containing complexes, for example with the irons of hemoproteins.⁶³ The similarity of its LUMO with the π^* orbitals of free NO strongly suggests that some similar metal-ligand bonding interactions are at work in the binding to metals of these two ligands.⁶⁴

IV. CALCULATED ENERGIES

For the QMC calculations, we used RHF/cc-pVTZ orbitals generated at the B3LYP/cc-pVTZ optimized geometry.^{57,65} Ground state energy calculations with each of the above methods at their respective optimized structures revealed a specific ordering of total valence energies calculated by RHF, MP2, and B3LYP, as well as VMC and DMC. The ordering of the energies in Table III is typical for this group of methods.

Although the VMC and DMC calculations used RHF orbitals with a cc-pVTZ basis, the QMC results only have a small, indirect basis set dependence. Basis set effects in DMC are limited to instances of poor description of the orbitals from traditional *ab initio* techniques. In order to guarantee effective orbital descriptions, we used either large basis sets or custom bases that have been developed to work well in DMC calculations. We also included a VMC valence energy for the SBK-ECP for comparison with a soft ECP developed by one of us (L.M.). As mentioned above, the soft ECPs are more stable and provide slightly lower energies. The increased efficiency of the soft ECP can be observed by comparing the error bars of the VMC calculations: 0.0025

TABLE II. NBO atomic charge densities of ONOO⁻ (cc-pVTZ basis).

	B3LYP	MP2
O1	-0.457	-0.419
N1	+0.196	+0.174
O2	-0.142	-0.087
O3	-0.598	-0.667

TABLE III. Valence energies of ONOO⁻ (hartree).

Method	6-311+G*	cc-pVTZ	aug-cc-pVTZ
RHF	-56.670 29	-56.717 48	-56.732 53
MP2	-57.484 05	-57.655 72	-57.702 77
B3LYP	-57.820 00	-57.853 68	-57.875 57
VMC/SBK ECP		-57.5005(25) ^a	
VMC/soft ECP		-57.5111(10) ^a	
DMC/soft ECP		-57.8509(9) ^a	

^aTruncated cc-pVTZ basis set without *F* functions.

Hartree (SBK) and 0.0010 Hartree (soft). These statistics are for equivalent computer time; halving the error in the VMC calculation with the SBK ECPs would require about four times more computational effort. The increased efficiency is the reason we restricted use to only the soft ECPs in the DMC calculations. Soft ECPs suitable for QMC have recently been extended to Be through Ne and Al through Ar.⁶⁶

We used the following expression to estimate the atomization energy (E_a) of peroxyntirite in VMC and DMC,

$$E_a = E(\text{O}^-) + 2E(\text{O}) + E(\text{N}) - [E(\text{ONOO}^-) - \text{ZPE}], \quad (10)$$

where E is the Monte Carlo valence energy of the indicated species, and ZPE is the zero-point vibrational energy determined by theory. We used an identical construction for the atomization energy estimates in the all-electron calculations for B3LYP, MP2, and RHF. While we computed energies for all species with and without the use of ECP's in the RHF, MP2, and B3LYP methods, we report the all-electron values in Table IV. The "valence" values reported in the other tables incorporate the ECP's of Stevens, Basch, and Krauss,⁶⁰ and are included as such to facilitate comparison to our ECP Monte Carlo energies. We find that the oxygen anion is a reasonable choice for the charged atomic species because it is more electronegative than nitrogen, and because of our use of the electron affinity of oxygen in computing an experimental atomization energy. This decision is also supported by examination of the results from the basis set methods, which consistently placed partial negative charges on the oxygens independent of the level of theory or basis set used (Table II). The experimental atomization energy was estimated by taking the difference of the heats of formation for the three atomic species from standard reference tables⁶⁷ and the heat of formation reported by Mereyni *et al.*⁶⁸ As shown in Table IV, atomization energies obtained with RHF,

TABLE IV. Atomization energies of ONOO⁻ (kcal/mol).

Method	6-311+G*	cc-pVTZ	aug-cc-pVTZ
All-electron RHF	62.65	78.19	69.63
All-electron MP2	267.11	290.84	282.99
All-electron B3LYP	286.01	287.03	276.02
VMC/soft ECP		204.0(1.8) ^a	
DMC/soft ECP		307.4(1.9) ^a	
Experiment ^b		313(1)	

^aTruncated cc-pVTZ basis set without *F* functions.^bReferences 67 and 68.TABLE V. Valence energies of O⁻ (hartree).

Method	6-311G*	6-311+G*	cc-pVTZ	aug-cc-pVTZ
ROHF	-15.590 00	-15.627 96	-15.617 95	-15.641 32
MP2	-15.752 16	-15.810 27	-15.825 70	-15.868 12
B3LYP	-15.856 35	-15.917 33	-15.893 80	-15.932 65
VMC			-15.8233(5) ^a	
DMC			-15.8854(8) ^a	

^aTruncated cc-pVTZ basis set without *F* functions.

MP2, B3LYP, and VMC yield estimates in poor accord with the experimental atomization energy. Good agreement, however, is obtained with DMC.

V. DISCUSSION

Calculated oxygen anion valence energies provide the clearest indicator of a potential source of error in estimating the atomization energy from *ab initio* wave function and GGA DFT methods for the present systems. Changing from the 6-311+G* (92 basis functions) to the larger cc-pVTZ (142 basis functions) unexpectedly *decreased* the valence energies calculated with ROHF and B3LYP (Table V). The generally expected effect of increasing the number of basis functions is a decrease in energy due to an improved ability to approximate the wave function of a given system. This unexpected basis set effect encountered in ROHF and B3LYP energies led us to investigate the specific role of the types, as opposed to the number, of basis functions. More specifically, additional calculations were performed using the 6-311G* and aug-cc-pVTZ bases to complete Table V and to investigate the effect of diffuse functions on the converged valence energies of O⁻ and ONOO⁻.

In Table VI we compare valence energy differences from calculations with the 6-311G* and 6-311+G* split-valence bases, and calculations with the cc-pVTZ and aug-cc-pVTZ bases. With the additional diffuse functions, the ROHF (B3LYP) energies for the oxygen anion in the split-valence bases were lowered by 0.039 (0.057) Hartree, whereas the peroxyntirite energies were lowered by 0.021 (0.033) Hartree. For the correlation consistent bases, oxygen anion energies decreased by 0.024 (0.038) Hartree and peroxyntirite energies by 0.014 (0.027) Hartree. Upon addition of diffuse functions, the MP2 energy decreases were roughly equal for O⁻ and ONOO⁻ in the correlation consistent bases. These findings, however, are consistent with reports that stress the need for diffuse orbitals when treating negative ions.^{69,70} Even though single point 6-311+G* calculations on

TABLE VI. Change in anion electronic energies due to addition of diffuse functions (hartree). $\Delta E_{\text{cc}} = E_{\text{aug-cc-pVTZ}} - E_{\text{cc-pVTZ}}$ ^a and $\Delta E_{\text{sv}} = E_{6-311+G^*} - E_{6-311G^*}$ ^b.

	$\Delta E_{\text{sv}}, \text{O}^-$	$\Delta E_{\text{cc}}, \text{O}^-$	$\Delta E_{\text{sv}}, \text{ONOO}^-$	$\Delta E_{\text{cc}}, \text{ONOO}^-$
RHF	-0.038 554	-0.023 829	-0.021 175	-0.014 166
MP2	-0.055 501	-0.043 883	-0.038 974	-0.046 126
B3LYP	-0.057 427	-0.037 638	-0.032 575	-0.026 744

^aThe "cc" subscript refers to "correlation consistent."^bThe "sv" subscript refers to "split-valence."

TABLE VII. Valence energies of oxygen and nitrogen atoms (hartree).

	O		N	
	6-311+G*	cc-pVTZ	6-311+G*	cc-pVTZ
ROHF	-15.646 47	-15.658 63	-9.630 54	-9.637 93
MP2	-15.772 97	-15.812 26	-9.717 10	-9.740 70
B3LYP	-15.862 73	-15.873 23	-9.765 39	-9.771 85
VMC	-15.8067(6) ^a		-9.7394(2) ^a	
DMC	-15.8524(4) ^a		-9.7613(5) ^a	

^aTruncated cc-pVTZ basis set without *F* functions.

ONOO⁻ included a smaller number of basis functions as compared to cc-pVTZ, our results strongly suggest that it is the presence of diffuse functions in the former basis set that mainly accounts for the improved energies of the anions studied. In fact, for neutral oxygen and nitrogen the energies were slightly lower for cc-pVTZ relative to 6-311+G*. This observation is also consistent with studies that report little effect of diffuse functions on some neutral molecules.⁷⁰ In addition, the energy differences due to basis set effects were consistent regardless of the presence of ECPs. Improvement due to diffuse functions differed in the third decimal place, with basis set effects being more pronounced in the valence calculations (Table VII).

VI. CONCLUSIONS

The RHF, MP2, B3LYP DFT, and DMC methods have been used to calculate the atomization energy of peroxy-nitrite anion. The DMC results are found to lie closest—within 5 kcal/mol—to the experimental value. We also found that the use of soft ECPs instead of the traditional SBK-ECPs provided substantial benefit by improving the overall efficiency of VMC and DMC calculations.

Atomization energy estimates from B3LYP and MP2, even with large basis sets, were in poor agreement with the experimental value. At the cc-pVTZ level, the MP2 and B3LYP methods underestimate the experimental value by approximately 25 kcal/mol and 40 kcal/mol, respectively. The atomization energy obtained with VMC was in particularly poor agreement. We attribute the underperformance of VMC to the use of a single-reference starting point for a system with multireference characteristics. At the same time, ROHF, MP2, and B3LYP valence energies of the oxygen anion showed a larger decrease than those of peroxy-nitrite upon addition of diffuse functions in the split-valence bases. This suggests that a main source of error when calculating atomization energies with these latter methods is the difference in improvement of the valence energies of the anions and atoms of Eq. (10) due to differences in levels of correlation energy recovered. Finally, our analysis of the valence energies reiterates the need for diffuse functions when treating negative ions such as O⁻ and ONOO⁻.

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