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Description	

Quantum Monte Carlo study of porphyrin transition metal complexes

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Diffusion quantum Monte Carlo (DMC) calculations for transition metal (M) porphyrin complexes (MPo , $M=Ni, Cu, Zn$) are reported. We calculate the binding energies of the transition metal atoms to the porphyrin molecule. Our DMC results are in reasonable agreement with those obtained from density functional theory calculations using the B3LYP hybrid exchange-correlation functional. Our study shows that such calculations are feasible with the DMC method. © 2008 American Institute of Physics. [DOI: 10.1063/1.2966003]

I. INTRODUCTION

Transition metal ions in biological molecules play a very important role in the field of bioinorganic chemistry¹ and organometallic chemistry.² Representative roles include the transport of oxygen,³ electron transfer,⁴ and the catalytic nature of metalloproteins,⁵ which are essential processes in metabolism.⁶ Electronic structure calculations of such systems are becoming more important in bio-based research fields, such as “drug design” in pharmaceuticals.

An accurate treatment of electron correlation in these systems with standard quantum chemistry techniques requires the use of multireference methods. Traditional quantum chemical multireference methods are not currently computationally feasible for such systems, which has stimulated interest in the density functional theory (DFT) approach.⁷ Although DFT is a powerful method for treating electronic correlations with a reasonable computational cost, its predictions often depend significantly on the specific choice of the exchange-correlation density functional.⁷ Calibrating such inconsistencies is one of the missions of the quantum Monte Carlo (QMC) method, which is a more reliable tool for calculating the energies of correlated electron systems.

It is vital to use pseudopotentials (also known as effective core potentials or ECPs) in QMC calculations for atoms with large atomic numbers Z because the computational cost is estimated to scale as $Z^{5.5-6.5}$.^{8,9} Pseudopotentials which are well suited for use in QMC calculations have recently been developed.^{10,11} Nonlocal exchange and correlation effects are very important for transition metal ions. It is therefore of technical interest to examine QMC pseudopotential calculations for systems including transition metal ions.

The first difficulty we face is the preparation of suitable basis sets for calculating the single particle orbitals used in the trial wave functions. Gaussian basis sets are commonly

used in biosystems, and popular ones include the Hay–Wadt (LANL1DZ, LANL2DZ) basis sets, which are designed for use with pseudopotentials.¹² However, the pseudopotentials commonly used in quantum chemistry calculations are not particularly suitable for QMC calculations because they diverge at the ionic centers. Such divergences lead to poor behavior in the local energy unless the proper cusp condition¹³ is applied. Orbitals expanded in a Gaussian basis set cannot satisfy the cusp condition, and the local energy then diverges at the ionic center and fluctuates wildly nearby, which leads to biases and even instabilities in diffusion quantum Monte Carlo (DMC) calculations. Although the cusp conditions at the ionic center may be enforced by modifying the Jastrow factor or correcting the orbitals,¹⁴ better results may be obtained by using pseudopotentials which are finite at the ionic center, such as those of Refs. 10 or 15. However, standard basis sets are not provided with these pseudopotentials, and therefore we have devised a simple scheme for generating Gaussian basis sets for them. We start with a standard Gaussian basis set for the Hay–Wadt pseudopotentials, and then optimize it for each molecule or atom by minimizing the energy within Hartree–Fock (HF) self-consistent field (SCF) calculations.

Porphyrin metal complexes are typical prosthetic groups of metalloproteins,¹⁶ such as the reaction centers of hemoglobin,¹⁷ vitamin B₁₂,¹⁸ etc. Electronic structure calculations for these complexes have been reported before.^{19–22} From the viewpoint of biochemistry, the existence of side chains is important, as it gives many possible combinations of side chain and transition metal ion (M) at the porphyrin center. Nevertheless, in the present study, we treat the porphyrin metal complex (MPo) without side chains, so that we can concentrate on the pseudopotential issues and avoid the complicated structural optimizations required for low-symmetry systems. Taking NiPo, CuPo, and ZnPo as examples, we evaluate the binding energy ΔE of the transition metal ion to the MPo . QMC calculations of electronic exci-

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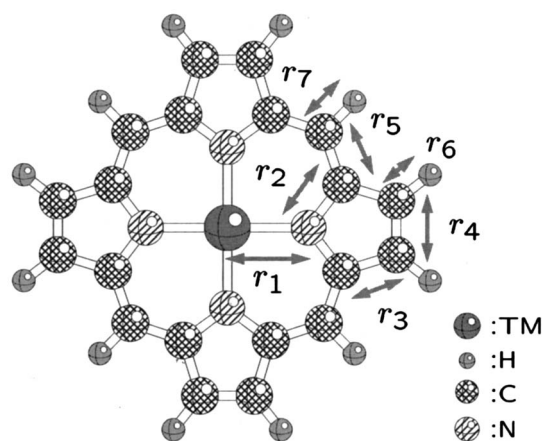


FIG. 1. Structure of the porphyrin metal complex, where $M = \text{Ni, Cu, Zn}$.

tations of the porphyrin molecule were reported by Aspuru-Guzik *et al.*,²³ who obtained excellent agreement with experiment, but we are not aware of any previous QMC calculations on *MPo*.

In this paper, we have calculated porphyrin metal complexes using the DMC method. The plan of this paper is as follows. In Sec. II, we describe the systems studied, and in Sec. III we describe the pseudopotentials and basis sets used in the calculations. The variational Monte Carlo (VMC) and DMC methods and calculations are described in Sec. IV. After giving the definition of the binding energy used here in Sec. V, the results of the calculations are reported and compared in Sec. VI. We draw our conclusions in Sec. VII.

II. STRUCTURES OF THE PORPHYRIN METAL COMPLEXES

The general porphyrin metal complex we have considered is shown in Fig. 1. The “FreeBase” (porphin without the two inner hydrogen atoms) and *MPo* structures were optimized within D_{4h} point group symmetry by performing all-electron (AE) B3LYP (Ref. 24) DFT calculations using 6-31G** Gaussian basis sets. Calculations of the vibrational frequencies of the molecules confirmed that the optimized structures for CuPo and ZnPo are stable. B3LYP and MP2 calculations gave an unstable vibrational mode for NiPo, and following the instability we obtained a structure of C_1 symmetry. We investigated this distortion further using the more sophisticated complete-active-space self-consistent-field (CASSCF) method, in which all possible configurations in an

active space [$N_{\text{occ}}, N_{\text{vir}}$] consisting of N_{occ} occupied and N_{vir} virtual orbitals are included. When we increased the active space from [2,2] to [6,6] (Ref. 25) the equilibrium structure returned to D_{4h} symmetry, showing that the C_1 distortion is an artifact.²⁰ We therefore employed the D_{4h} structure for NiPo as well. The bond lengths of the optimized structures are shown in Table I. All calculations were carried out using the *ab initio* quantum chemical package GAUSSIAN03.²⁶

III. PSEUDOPOTENTIALS AND BASIS SETS

We performed AE and pseudopotential calculations at the HFSCF and B3LYP levels, and QMC calculations using pseudopotentials. We used both large-core (Ar core) and small core (Ne core) pseudopotentials for the M . We have investigated the effects of varying the parameters of the calculations, including the size of the basis set. These results enable us to investigate the results obtained with different pseudopotentials, explore the convergence with respect to basis set size and study the differences obtained at different levels of theory.

We used the following combinations of AE /pseudopotentials and basis sets:

- AE; 6-31G**, cc-pvTZ(-NR),
- small core; LANL2DZ, CRENBL, SBKJC-VDZ,
- large core; LANL1DZ, CRENBS, TN_{pp}.

The cc-pvTZ (Ref. 27) (correlation consistent polarized valence triple zeta) basis sets are larger than the 6-31G** ones. LANL1DZ (LANL2DZ) denotes the Hay–Wadt large (small) core pseudopotentials for the transition metal ions with LANL1DZ (LANL2DZ) (=Hay-Wadt) basis sets.¹⁴ CRENBL (CRENBS) (Ref. 28) is a small (large) shape consistent pseudopotential which includes an averaged treatment of relativistic effects, and for which basis sets are provided. SBKJC-VDZ (Ref. 29) is a relativistic small core pseudopotential with basis sets supplied. TN_{pp} stands for the smooth large core HF pseudopotential of Trail and Needs.¹⁰ For the TN_{pp}, we used optimized LANL1DZ basis sets, and for the lighter atoms described by TN_{pp} pseudopotentials we used optimized 6-31G** basis sets. We optimized the exponents and contraction coefficients of the basis sets by approximately minimizing the HF-SCF energy. Tests have indicated that HFSCF orbitals are near optimal for *sp* atoms,^{30,31} al-

TABLE I. Optimized bond lengths in angstrom for each complex using B3LYP/6-31G**. The definitions of the bond lengths are shown in Fig. 1. FreeBase does not contain a transition metal atom, and in this case r_1 corresponds to half the distance between two N atoms on opposite sides of the ring.

		NiPo	CuPo	ZnPo	FreeBase
r_1	(M–N)	1.957	2.007	2.043	2.066
r_2	(N–C)	1.381	1.376	1.374	1.355
r_3	(C–C)	1.438	1.443	1.445	1.461
r_4	(C–C)	1.358	1.361	1.364	1.362
r_5	(C–C)	1.380	1.389	1.396	1.409
r_6	(C–H)	1.082	1.082	1.082	1.083
r_7	(C–H)	1.085	1.085	1.086	1.090

though they may not be as accurate for transition metal atoms. The basis sets optimizations were carried out separately for each molecule and atom considered. QMC calculations were performed using the TN_pp for both the transition metal ion and FreeBase, with optimized LANL1DZ basis sets.

IV. VMC AND DMC METHODS

The VMC energy is evaluated as the expectation value of the Hamiltonian \hat{H} with a many-body trial wave function Ψ ,

$$E = \frac{\int \Psi^* \hat{H} \Psi d\mathbf{R}}{\int \Psi^* \Psi d\mathbf{R}} = \frac{\int |\Psi|^2 \Psi^{-1} \hat{H} \Psi d\mathbf{R}}{\int |\Psi|^2 d\mathbf{R}}, \quad (1)$$

where \mathbf{R} is the $3N$ -dimensional vector of the electron positions, and the energy has been written as an average of the “local energy” $E_L = \Psi^{-1} \hat{H} \Psi$ over the probability distribution $p(\mathbf{R}) = |\Psi|^2 / \int |\Psi|^2 d\mathbf{R}$. The energy expectation value is evaluated by Monte Carlo integration, using the Metropolis algorithm to generate electronic configurations distributed according to $p(\mathbf{R})$. The statistical efficiency of the Monte Carlo integration improves as the quality of Ψ improves because $E_L = \Psi^{-1} \hat{H} \Psi$ becomes a smoother function of \mathbf{R} .

All of the QMC calculations were performed with the CASINO QMC code.³² We first performed VMC calculations using a trial wave function consisting of the product of up and down-spin determinants of the HFSCF orbitals,

$$\Psi(\mathbf{R}) = D_{\uparrow}(\mathbf{R}) D_{\downarrow}(\mathbf{R}). \quad (2)$$

When using the pseudopotentials which diverge at the ion center, we have forced the molecular orbitals to satisfy the proper cusp condition at each ionic center using the procedure introduced by Ma *et al.*¹⁴ The radial part of each molecular orbital is replaced by a form with the required cusp inside some small radius around the ionic center and smoothly connected to the Gaussian orbitals outside. The cusp corrected molecular orbitals lower the VMC energy and reduce the standard error in the energy by a factor of about 10. The cusp correction procedure is not required for the TN-pp pseudopotentials, and the calculations with these pseudopotentials reproduce the HFSCF results to within statistical error bars.

In the VMC calculations with Slater–Jastrow wave functions, the trial functions took the form

$$\Psi(\mathbf{R}) = \exp[J(\mathbf{R})] D_{\uparrow}(\mathbf{R}) D_{\downarrow}(\mathbf{R}), \quad (3)$$

where $\exp[J(\mathbf{R})]$ is a Jastrow correlation factor. Where necessary, we used the cusp corrected HFSCF orbitals described above to form the determinants D_{\uparrow} and D_{\downarrow} . The Jastrow factors took the form³³

$$J(\mathbf{R}) = \sum_{i>j} u(r_{ij}) + \sum_I \sum_i \chi_I(r_{iI}) + \sum_I \sum_{i>j} f_I(r_{iI}, r_{jI}, r_{ij}), \quad (4)$$

where i and j denote electrons and I denotes ions. The u term describes homogeneous, isotropic, electron-electron correlations, the χ term one-body isotropic electron-nucleus correlations, and the f term isotropic electron-electron-nucleus correlations. The terms are represented as power series in

their arguments, constrained to enforce the electron-electron cusp conditions while maintaining the electron-nucleus cusp conditions. The coefficients in the power expansions are determined by minimizing the self-consistent unweighted variance of the energy using a VMC procedure. As the coefficients appear linearly in the Jastrow factor, the optimization can be performed efficiently using the scheme devised by Drummond *et al.*³⁴

In the DMC method, the ground-state component of a trial wave function is projected out by evolving an ensemble of electronic configurations using the imaginary-time Schrödinger equation. Attempts to carry out this procedure exactly result in a “fermion sign problem,” which is removed by constraining the nodal surface of the wave function (the surface in configuration space on which the wave function is zero and across which it changes sign) to equal that of the trial wave function. The DMC energy calculated with this fixed-node constraint is higher than the exact ground-state energy, and becomes equal to it when the fixed nodal surface is exact.

We used the optimized Slater–Jastrow wave functions as trial functions for the DMC calculations. Time steps of 0.01 and 0.001 a.u. were used for the DMC calculations. In the atomic DMC calculations, we used an average population size of 1000 configurations, while in the MPo and Po calculations we used an average population size of 8000 configurations, which are expected to lead to negligible population control errors. Furthermore, population control errors tend to cancel in energy differences because they always increase the energy.^{35,36}

V. DEFINITION OF THE BINDING ENERGY

We evaluate the energy difference between the neutral states,

$$\Delta E = [E(\text{Free Base}) + E(M)] - E(\text{MPo}), \quad (5)$$

which requires the energies of FreeBase [$E(\text{FreeBase})$], the neutral atomic energy for the M [$E(M)$], and the energy of MPo [$E(\text{MPo})$]. We can use this quantity to compare the results of the pseudopotential and AE calculations. We note that the quantity

$$[E(\text{Po}^{2-}) + E(M^{2+})] - E(\text{MPo}) \quad (6)$$

is often studied in experimental syntheses in aqueous solution because the ionic states, $X^{2\pm}$, are much more stable than the neutral states due to the solvation by water molecules. Since we have assumed isolated MPo systems, we have not evaluated this quantity here.

VI. RESULTS

The calculated binding energies ΔE for NiPo, CuPo, and ZnPo are given in Tables II–IV, respectively. We found that the HFSCF results for CuPo were sensitive to the initial guess, and we experimented with a number of initial guesses in order to achieve satisfactory results. The differences between the AE results obtained with the 6-31G** and cc-pvTZ-NR transition metal basis sets are as large as 0.13 a.u., and we conclude that the 6-31G** transition metal

TABLE II. Comparison of ΔE (atomic units) from different methods for NiPo.

	Transition metal	FreeBase	Method	ΔE
AE	6-31G**	6-31G**	HFSCF	0.301
AE	cc-pvTZ-NR	6-31G**	HFSCF	0.310
AE	cc-pvTZ-NR	cc-pvTZ	HFSCF	0.309
AE	6-31G**	6-31G**	B3LYP	0.406
AE	cc-pvTZ-NR	6-31G**	B3LYP	0.321
AE	cc-pvTZ-NR	cc-pvTZ	B3LYP	0.341
Small core	LANL2DZ	cc-pvTZ	HFSCF	0.307
Small core	LANL2DZ	6-31G**	HFSCF	0.305
Small core	CRENBL	6-31G**	HFSCF	0.307
Small core	SBKJC VDZ	6-31G**	HFSCF	0.311
Small core	LANL2DZ	cc-pvTZ	B3LYP	0.338
Small core	LANL2DZ	6-31G**	B3LYP	0.314
Small core	CRENBL	6-31G**	B3LYP	0.306
Small core	SBKJC VDZ	6-31G**	B3LYP	0.320
Large core	LANL1DZ	6-31G**	HFSCF	0.283
Large core	CRENBS	6-31G**	HFSCF	0.442
Large core	TN_pp	6-31G**	HFSCF	0.225
Large core	TN_pp	TN_pp	HFSCF	0.226
Large core	LANL1DZ	6-31G**	B3LYP	0.243
Large core	CRENBS	6-31G**	B3LYP	0.266
Large core	TN_pp	6-31G**	B3LYP	0.271
Large core	TN_pp	TN_pp	B3LYP	0.292
Large core	TN_pp	6-31G**	DMC ($\delta t=0.01$)	0.375(2)
Large core	TN_pp	TN_pp	DMC ($\delta t=0.001$)	0.32(2)
Large core	TN_pp	TN_pp	DMC ($\delta t=0.01$)	0.333(1)

TABLE III. Comparison of ΔE (atomic units) from different methods for CuPo.

	Transition metal	FreeBase	Method	ΔE
AE	6-31G**	6-31G**	HFSCF	0.356
AE	cc-pvTZ-NR	6-31G**	HFSCF	0.321
AE	cc-pvTZ-NR	cc-pvTZ	HFSCF	0.320
AE	6-31G**	6-31G**	B3LYP	0.399
AE	cc-pvTZ-NR	6-31G**	B3LYP	0.269
AE	cc-pvTZ-NR	cc-pvTZ	B3LYP	0.289
Small core	LANL2DZ	cc-pvTZ	HFSCF	0.311
Small core	LANL2DZ	6-31G**	HFSCF	0.310
Small core	CRENBL	6-31G**	HFSCF	0.311
Small core	SBKJC VDZ	6-31G**	HFSCF	0.318
Small core	LANL2DZ	cc-pvTZ	B3LYP	0.286
Small core	LANL2DZ	6-31G**	B3LYP	0.529
Small core	CRENBL	6-31G**	B3LYP	0.257
Small core	SBKJC VDZ	6-31G**	B3LYP	0.269
Large core	LANL1DZ	6-31G**	HFSCF	0.298
Large core	CRENBS	6-31G**	HFSCF	0.228
Large core	TN_pp	6-31G**	HFSCF	0.293
Large core	TN_pp	TN_pp	HFSCF	0.293
Large core	LANL1DZ	6-31G**	B3LYP	0.196
Large core	CRENBS	6-31G**	B3LYP	0.162
Large core	TN_pp	6-31G**	B3LYP	0.240
Large core	TN_pp	TN_pp	B3LYP	0.255
Large core	TN_pp	6-31G**	DMC ($\delta t=0.01$)	0.249(2)
Large core	TN_pp	TN_pp	DMC ($\delta t=0.001$)	0.237(7)
Large core	TN_pp	TN_pp	DMC ($\delta t=0.01$)	0.230(1)

TABLE IV. Comparison of ΔE (atomic units) from different methods for ZuPo.

	Transition metal	FreeBase	Method	ΔE
AE	6-31G**	6-31G**	HFSCF	0.307
AE	cc-pvTZ-NR	6-31G**	HFSCF	0.274
AE	cc-pvTZ-NR	cc-pvTZ	HFSCF	0.272
AE	6-31G**	6-31G**	B3LYP	0.316
AE	cc-pvTZ-NR	6-31G**	B3LYP	0.237
AE	cc-pvTZ-NR	cc-pvTZ	B3LYP	0.257
Small core	CRENBL	6-31G**	HFSCF	0.252
Small core	SBKJC VDZ	6-31G**	HFSCF	0.266
Small core	CRENBL	6-31G**	B3LYP	0.207
Small core	SBKJC VDZ	6-31G**	B3LYP	0.229
Large core	LANL1DZ	6-31G**	HFSCF	0.272
Large core	CRENBS	6-31G**	HFSCF	0.232
Large core	TN_pp	6-31G**	HFSCF	0.237
Large core	TN_pp	TN_pp	HFSCF	0.237
Large core	LANL1DZ	6-31G**	B3LYP	0.240
Large core	CRENBS	6-31G**	B3LYP	0.198
Large core	TN_pp	6-31G**	B3LYP	0.252
Large core	TN_pp	TN_pp	B3LYP	0.273
Large core	TN_pp	6-31G**	DMC ($\delta t=0.01$)	0.262(2)
Large core	TN_pp	TN_pp	DMC ($\delta t=0.001$)	0.266(8)
Large core	TN_pp	TN_pp	DMC ($\delta t=0.01$)	0.265(1)

basis set is inadequate for these calculations. The differences between the AE results obtained with the 6-31G** and cc-pvTZ FreeBase basis sets are 0.02 a.u. or less, and we conclude that the 6-31G** basis is adequate for the AE C, N, and H atoms. The pseudopotential results do not depend strongly on the choice of basis set, except for the curious case of CuPo with the small core LANL pseudopotential and 6-31G** FreeBase basis set within B3LYP. With the exception of this case, our results provide good evidence that the pseudopotential binding energies with the larger basis sets are well converged. The DMC results do not appear to be very sensitive to the basis set used.

The larger basis set AE results are in reasonable agreement with the small core pseudopotential results. The results with small core pseudopotentials are in fairly good agreement with one another, except for the exceptional CuPo case. There is a tendency for the large core pseudopotential binding energies of NiPo and CuPo to be somewhat smaller than the small core ones. Presumably this is due to the additional approximation of treating the $3s$ and $3p$ electrons within the pseudopotential. The agreement between the various large core results is not as good as for the small core ones, indicating sensitivity to the form of the pseudopotential.

We found the DMC calculations to be unstable with the LANL pseudopotentials which diverge at the origin, but they were stable with the smooth TN-pp pseudopotentials. Due to the large computational cost of the calculations, the statistical error bars obtained with a time step of 0.001 a.u. are considerably larger than those obtained with a time step of 0.01 a.u. The energies obtained with the two time steps are within statistical errors of one another, indicating that the time step errors are not larger than the error bars. The DMC binding energy of CuPo is larger than the HFSCF and B3LYP values obtained with the same pseudopotentials, in-

dicating the importance of an accurate description of valence correlation for this system. The DMC binding energies of NiPo and ZnPo are similar to the HFSCF and B3LYP values obtained using the same pseudopotentials.

Liao and Scheiner²³ have reported DFT results for *M*Po structures with four phenyl side chains and for the same model *M*Po system that we have used. Our geometries are in good agreement with theirs, with a maximum deviation in *M*-N bond length of 1.1% for CuPo. They used a frozen core approximation, which is roughly equivalent to using small core pseudopotentials, and so our LANL small core binding energies should be comparable with theirs. We find quite good agreement with our B3LYP-DFT results, with a maximum deviation in the binding energy of 0.032 a.u. for ZnPo.

VII. CONCLUSION

We have performed calculations for transition metal atoms, porphin and porphyrin *M* complexes using a variety of methods. AE and pseudopotential methods were used, including both small and large core transition metal pseudopotentials. DMC calculations were only feasible with large core transition metal pseudopotentials. The DMC calculations with pseudopotentials that diverge at the origin were unstable, but they were stable when the nondivergent TN-pp pseudopotentials were used. We calculated the binding energy of the transition metal ion to the porphin. There are significant variations between the binding energies calculated with the B3LYP, HFSCF, and DMC methods, and with the different AE and pseudopotential treatments. The results are insensitive to whether the C, N and H atoms are treated with AE or pseudopotential methods, but they depend significantly on the treatment of the *M*. Comparisons between our small and large core results and the DFT calculations of Liao and Scheiner²³ suggest that small core *M* pseudopotentials are required to obtain accurate results, particularly for CuPo and NiPo. We found reasonable agreement between our DFT binding energies and those of Liao and Scheiner.²³ Our study has demonstrated that DMC calculations for *M*Po systems are possible.

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