

Accurate quantum Monte Carlo calculations for hydrogen fluoride and the fluorine atom

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Quantum Monte Carlo calculations of the ground state energies of the fluorine atom and the hydrogen fluoride molecule have been carried out using both fixed-node and released-node methods. The fixed-node total energies for both F and FH are among the most accurate available. The fixed-node dissociation energy $D_e=141.3(4)$ kcal mol⁻¹ is in excellent agreement with experimental data. The cancellation of the nodal error was achieved with trial wave functions having nodal surfaces determined by Slater determinants of the near Hartree–Fock limit quality. With the released-node Green’s function quantum Monte Carlo method the lowest upper bounds to the ground state energies to date for both F [$E_0=-99.731(4)$ Hartree] and FH [$E_0=-100.458(5)$ Hartree] have been obtained. © 1996 American Institute of Physics. [S0021-9606(96)00935-X]

I. INTRODUCTION

The quantum Monte Carlo method has been successful in calculating accurately the ground state energy and other properties of many atoms and molecules.^{1–3} For few-electron systems such as H₂, H₃, and LiH, quantum Monte Carlo methods provide exact solutions of the Schrödinger equation.¹ For larger systems, quantum Monte Carlo methods do not at present provide exact solutions, but they do provide highly accurate solutions.²

In this paper we report accurate QMC calculations for the F atom and the FH molecule. Two methods have been used: the fixed-node diffusion quantum Monte Carlo (FN-DQMC) and the released-node Green’s function quantum Monte Carlo (RN-GFQMC), to obtain accurate total energies for each species and an accurate dissociation energy for FH. The results indicate the magnitude of the nodal errors and their effects on the accuracy of the calculated dissociation energy.

More than 90% of the correlation energy can be obtained for a ten-electron system like FH using the fixed-node approximation⁴ in which the nodes of a trial wave function are imposed on the solution of the Schrödinger equation. Since the remaining part of the correlation energy, the nodal error, is of the order of 10 kcal mol⁻¹ for hydrogen fluoride, the calculation of the dissociation energy and other energy differences with a chemical accuracy better than 1 kcal mol⁻¹ remains a challenge for QMC methods. The accurate determination of energy differences like the dissociation energy depends on an efficient cancellation of the nodal error, making it important to control the nodal error. The effects of the nodal error have been investigated in only a few studies.^{5,6}

The nodal error may be avoided with the use of the RN-GFQMC method.^{7,8} In principle, this method allows the exact determination of the ground state energy, but in practice it is currently difficult to obtain error bars of the order of the chemical accuracy for systems with more than about six electrons. We have applied the RN-GFQMC method to both F and FH.

II. FIXED-NODE QUANTUM MONTE CARLO METHOD

The basis for the diffusion quantum Monte Carlo method (DQMC) is the time-dependent Schrödinger equation in imaginary time,

$$\frac{\partial \Psi}{\partial \tau} = -H\Psi = \frac{1}{2} \nabla^2 \Psi - V\Psi. \quad (1)$$

The stationary solution of this equation is the ground state wave function Ψ_0 . This equation is mathematically a diffusion equation and it can be simulated with a random walk of particles leading to a sample with a distribution of the stationary solution Ψ_0 .

Because of the Pauli principle the ground state wave function for an electron system with more than two electrons has a nodal hypersurface and is thus not the stationary solution of Eq. (1). The Pauli principle can be satisfied by imposing an appropriate nodal hypersurface on the stationary solution and solving Eq. (1) with the nodal hypersurface as an additional boundary condition. Since the nodal hypersurface is not fully determined by the Pauli principle the stationary solution will in general be only an approximation to the exact wave function, and it can be shown that the corresponding eigenvalue is an upper bound to the exact nonrelativistic eigenvalue.¹⁰ The difference is known as the *nodal error* and is dependent solely on the nodal hypersurface.

An approximate nodal hypersurface is most easily defined by the nodes of a trial wave function Ψ_T that satisfies the Pauli principle. The ground state Ψ_0^{FN} within each nodal region of Ψ_T is then nodeless and thus the product of Ψ_0^{FN} with the trial function $f=\Psi_0^{\text{FN}}\Psi_T$ is positive. Transforming Eq. (1) into an equation for f , interpreted as a probability density, is possible by multiplying Eq. (1) by Ψ_T and rearranging to obtain¹⁰

$$\frac{\partial f}{\partial \tau} = \frac{1}{2} \nabla^2 f - \nabla[f\nabla \ln|\Psi_T|] - [E_{\text{loc}} - E_T]f, \quad (2)$$

with the local energy $E_{\text{loc}}=H\Psi_T/\Psi_T$, which is a function of the position in configuration space. This equation can be simulated with a random walk composed of a diffusion, a

drift, and a branching or weighting step.¹⁰ The nodes can be enforced by rejecting all moves that attempt to cross a node of Ψ_T . The fixed-node ground state energy E_0^{FN} can then be obtained as the expectation value of the local energy over the stationary distribution $p(\mathbf{R}) = \Psi_0^{\text{FN}} \Psi_T / \int \Psi_0^{\text{FN}} \Psi_T d\mathbf{R}$. Thus, we have

$$E_0^{\text{FN}} = \int E_{\text{loc}}(\mathbf{R}) p(\mathbf{R}) d\mathbf{R} = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{i=1}^N E_{\text{loc}}(\mathbf{R}_i), \quad (3)$$

where \mathbf{R} denotes a position vector in configuration space and E_0^{FN} the ground state energy for the Schrödinger equation, with the additional boundary condition of vanishing Ψ at the nodes defined by the trial function Ψ_T . Besides the nodal error, Ψ_T also controls the statistical variance of the random walk calculation of E_0^{FN} . As can be seen directly from Eq. (3), the variance approaches zero as Ψ_T approaches the exact ground state wave function Ψ_0 . Expectation values can be obtained similarly.

The random walk simulation of Eq. (2) requires a discretization of the imaginary time τ . The use of finite time steps introduces a *time step error* that can be eliminated by extrapolating to time step $\tau \rightarrow 0$. For the calculations of this paper we used the algorithm by Reynolds, *et al.*¹⁰ A modified algorithm with reduced time step error has been given by Umrigar, Nightingale, and Runge.¹¹

III. RELEASED-NODE GREEN'S FUNCTION QUANTUM MONTE CARLO

With the released-node Green's function quantum Monte Carlo method both types of errors mentioned in the last section, the nodal error and the time-step error, can be avoided. The basic formulas are given by a rearrangement of the time-independent Schrödinger equation for the ground state,

$$-\frac{1}{2}\nabla^2\Psi_0 + V\Psi_0 = E_0\Psi_0, \quad (4)$$

to obtain

$$-\nabla^2\Psi(\mathbf{R}) + k^2\Psi(\mathbf{R}) = k^2 \frac{V(\mathbf{R})}{E_0} \Psi(\mathbf{R}), \quad (5)$$

with $k^2 = -2E_0$. The Green's function corresponding to the left side is known for the boundary condition $\Psi(\mathbf{R}) \rightarrow 0$ as $R \rightarrow \infty$ and given by

$$G_0(\mathbf{R}, \mathbf{R}') = (2\pi)^{-3N/2} (k|\mathbf{R} - \mathbf{R}'|)^{1-3N/2} \times K_{3N/2-1}(k|\mathbf{R} - \mathbf{R}'|), \quad (6)$$

where K_ν is the modified Bessel function of the second kind. The integral equation corresponding to Eq. (5) is thus

$$\Psi(\mathbf{R}) = \int d\mathbf{R}' G_0(\mathbf{R}, \mathbf{R}') \frac{V(\mathbf{R}')}{E_0} \Psi(\mathbf{R}'). \quad (7)$$

The iteration of this integral equation can be simulated with a random walk process, where $G_0(\mathbf{R}, \mathbf{R}')$ represents the transition matrix and $V(\mathbf{R}')/E_0$ an additional weighting step.^{7,8} Unfortunately, the eigenfunction with the lowest eigenvalue of Eq. (7) is not Ψ_0 for systems with nodes.

Although the iteration of Eq. (7) with an initial trial wave function leads to a decay of the contribution from excited wave functions, the electronic ground state wave function Ψ_0 decays to a nodeless, or "boson," ground state. While the energy of the antisymmetric state can be projected out with an antisymmetric trial wave function in the mixed estimator,

$$E_0 = \frac{\langle \Psi_0 | H \Psi_T \rangle}{\langle \Psi_0 | \Psi_T \rangle}, \quad (8)$$

the uncertainty in the energy increases rapidly with the number of iterations. In this way we obtain a transient estimator yielding upper bounds that converge toward the exact ground state energy E_0 with increasing iterations. For systems with three or four electrons this process can be stabilized by a cancellation procedure.¹⁴

The actual realization in this work differs from previous calculations.^{15,9} In order to avoid any additional bias by killing particles after a given number of iterations, we simply count as generations each realization of an iteration step of Eq. (7). The initial samples of particles for the released-node runs are taken from FN-DQMC calculations with small time steps. In practice, we carry out a FN-DQMC calculation, and after the initial equilibration we take successive independent weighted samples from the fixed-node distribution as initial samples for the GFQMC iterations. In this form, the RN-GFQMC calculations appear as *sidewalks* from a main fixed-node random walk process. Weighting and branching in the GFQMC is carried out as in previous work.⁹

IV. RESULTS

The trial wave functions Ψ_T used in this work consist of the usual product of determinants for the α and β electrons with a Jastrow factor,

$$\Psi_T = \det \Phi^{(\alpha)} \det \Phi^{(\beta)} e^U, \quad U = \sum_{a,i < j} U_{a,i,j}, \quad (9)$$

where Φ is an orbital product and $U_{a,i,j}$ a correlation factor. We employed a form of $U_{a,i,j}$ given by Schmidt and Moskowitz¹³ that has been developed by Boys and Handy for transcorrelated wave functions,¹²

$$U_{a,i,j} = \sum_k^{N_a} c_{ka} (r_{ai}^{-l_{ka}} r_{aj}^{-m_{ka}} + r_{aj}^{-l_{ka}} r_{ai}^{-m_{ka}}) r_{ij}^{-n_{ka}}, \quad (10)$$

TABLE I. Time step dependence of FN-DQMC energies for F and FH ground states.

Time step (Hartree ⁻¹)	Energy (F) Hartree	Energy (FH) Hartree
0.001	-99.7174(4)	-100.4423(6)
0.002	-99.7172(4)	-100.4431(5)
0.005	-99.7198(3)	-100.4438(5)
0.007	-99.7230(4)	-100.4472(7)
0.010	-99.7330(4)	-100.4530(7)
0.012	-99.7424(4)	-100.4589(12)
0.015	-99.7600(7)	-100.4679(11)

TABLE II. Selected results for the 2P ground state energy of the fluorine.

Total energy (Hartree)	Correlation energy (%)	Method	Authors
-99.409 35		HF limit	Davidson <i>et al.</i> (1991) Ref. 26
-99.734		Nonrelativistic limit	Davidson <i>et al.</i> (1991) Ref. 26
-99.7166	95	CI-SDTQ	Sasaki/Yoshimine (1974) Ref. 27
-99.7128	94	CCSD+T	Adamowicz/Bartlett (1986) Ref. 28
-99.719	95	CCSD(T)	Scuseria (1993) Ref. 29
-99.669(1)	80	VQMC	Schmidt/Moskowitz (1990) Ref. 13
-99.7005(21)	90	FN-DQMC	Barnett/Reynolds/Lester (1986) Ref. 19
-99.7178(6)	95	FN-DQMC	Garner/Anderson (1988) Ref. 20
-99.7176(3)	95	FN-DQMC	This work
-99.731(4)	100	RN-GFQMC	This work

where a and i, j refer to the nuclei and the electrons, respectively, and where \bar{r} is defined by $\bar{r} = br / (1 + br)$. The nodes of this function, and thus the nodal error, are solely dependent on the orbitals.

We used an STO basis set of the type $(5s, 4p, 2d/3s, 2p)$ for FH and $(6s, 4p)$ for F with near HF limit results. For F the Slater determinant was taken from Clementi and Roetti,¹⁶ and for FH we slightly simplified a basis set from Cade and Huo¹⁷ by neglecting f -type functions and by using the same exponents for σ and π orbitals. The MOs were then obtained with GAMESS.¹⁸ The Jastrow function e^U for the F atom with nine terms in Eq. (10) was taken from Schmidt and Moskowitz¹³ and a comparable 14-term Jastrow function for FH was optimized by variance minimization similarly to Ref. 13. The resulting explicitly correlated wave function is capable of obtaining about 80% of the correlation energy in a variational Monte Carlo calculation (VQMC) for both F and FH (Tables II and III).

To eliminate the time step error we used different time steps and a quadratic extrapolation to $\tau=0$. The individual data are given in Table I.

When using this type of trial wave function we observed a strong dependence of the nodal error on the quality of the molecular orbitals. While a nodal error of 34 mHartree has been found by Barnett, Reynolds, and Lester¹⁹ for a double-zeta STO wavefunction for the F atom, we obtain a nodal error of only 16 mHartree for a near HF-limit Slater deter-

minant (Table II). Similarly, we could reduce the nodal error for hydrogen fluoride compared to that for an extended basis set calculation of Garner and Anderson²⁰ by 4 mHartree to obtain a nodal error of only 16 mHartree. This could be achieved by using again a near HF-limit Slater determinant. The total fixed-node energy is among the best available for the FH molecule (Table III).

With these accurate calculations we obtain a dissociation energy $D_e = 141.3(4)$ kcal mol⁻¹. The nonrelativistic experimental value of 141.51 kcal mol⁻¹ is obtained by correcting the experimental dissociation energy²¹ for spin-orbit effects.²² Our result is in excellent agreement with this value, and it is remarkable for its virtually perfect cancellation of the nodal error. It can be matched only by the most sophisticated analytical calculations (Table IV).

The accuracy of energy differences like the dissociation energy obtained with the fixed-node method depends on the extent of cancellation of the nodal errors. We would like to point out that a well-defined nodal surface like the one defined by the SCF-MOs of a given basis set is desirable for an investigation of the cancellation. Other possibilities may be natural orbitals or a small MCSCF wavefunction from an analytic calculation. QMC methods have been used to optimize the MOs or the CI coefficients of a multiconfiguration wave function with respect to the variance, but a reduction of the variance does not necessarily cause a reduction of the nodal error.²³ Additionally, the variance minimization is a

TABLE III. Selected results for the $^1\Sigma^+$ ground state energy of hydrogen fluoride at the equilibrium distance $R_e = 1.733$ bohr.

Total energy (Hartree)	Correlation energy (%)	Method	Authors
-100.071 85		HF limit	Peterson/Kendall/Dunning (1993) Ref. 22
-100.460		Nonrelativistic limit	This work
-100.4470	97	CCSD+T(CCSD)	Adamowicz/Bartlett (1988) Ref. 30
-100.4131	88	CCSD(T)	Kraka/Gauss/Cremer (1993) Ref. 31
-100.3866	81	CCSD(T)	Peterson/Dunning (1995) Ref. 32
-100.375(2)	78	VQMC	This work
-100.4385(22)	94	FN-DQMC	Garner/Anderson (1988) Ref. 20
-100.4429(6)	96	FN-DQMC	This work
-100.458(5)	100	RN-GFMC	This work

TABLE IV. Selected results for the dissociation energy D_e of hydrogen fluoride.

D_e (kcal mol ⁻¹)	Method	Authors
141.13	Experimental	Zemke <i>et al.</i> (1991) Ref. 21
141.51	Experimental	with spin-orbit correction
141.8	CCSD(T)	Bartlett (1989) Ref. 33
140.7	CCSD(T)	Kraka/Gauss/Cremer Ref. 31
140.9	CCSD(T)	Scuseria (1993) Ref. 29
141.3	CCSD(T)	Peterson/Dunning (1995) Ref. 32
141.2	MRCI+Q	Stark/Werner Ref. 34
130(1)	VQMC	This work
138(1)	FN-DQMC	Garmer/Anderson (1988) Ref. 20
141.3(4)	FN-DQMC	This work
142(4)	RN-GFQMC	This work

TABLE V. RN-GFQMC energies for the F and FH ground states given for successive generations with error bars.

Generation	Energy (F) Hartree	Energy (FH) Hartree
1	-99.7129(9)	-100.431(1)
2	-99.715(1)	-100.430(2)
3	-99.715(1)	-100.432(3)
4	-99.716(2)	-100.434(3)
5	-99.721(2)	-100.429(4)
6	-99.716(2)	-100.439(4)
7	-99.722(3)	-100.442(5)
8	-99.731(4)	-100.458(5)
9	-99.739(6)	-100.459(7)
10	-99.739(12)	-100.461(11)

nonlinear problem with many parameters. Typically, there will be many shallow local minima, making the nodal error dependent on the optimization procedure and the random samples if the MOs are to be optimized.

Dissociation energies can also be obtained from variational quantum Monte Carlo (VQMC) calculations, but the dissociation energy calculated from the VQMC energies in this work, $D_e = 130(1)$ kcal mol⁻¹, is considerably less accurate. The VQMC energies, like the nodal error in the case of MO optimization, are dependent on the stochastic variance minimization, and the variational energy, like the nodal error, is not necessarily a monotonous function of the variance.

In Fig. 1 the fixed-node energies for several internuclear distances are shown together with the experimental potential energy curve as constructed from vibrational energy levels with the Rydberg, Klein, Rees (RKR) method.²⁴ The fixed-node curve appears to be quite accurate in the vicinity of the equilibrium distance, although the error bars do not allow an accurate determination of the spectroscopic constants. For large separations the fixed-node energies are too high. This is not surprising as SCF-type wave functions show an incorrect dissociation behavior and so do their nodes that determine

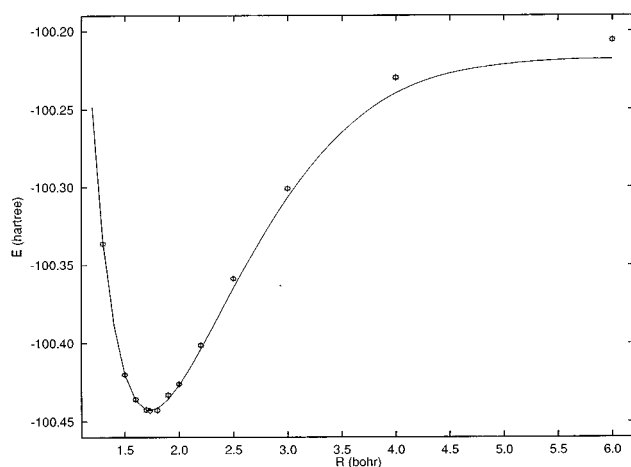


FIG. 1. FN-DQMC calculations for different nuclear distances are shown with error bars, together with the experimental potential energy curve.

the fixed-node energy. GVB or MCSCF wave functions are necessary in fixed-node calculations if a full potential energy curve is to be calculated accurately.

For the released-node GFQMC calculations, we used the same trial wavefunction as for the fixed-node calculation in the case of the F atom and a simpler function of the same type for FH. In Table V the averaged energies for the individual generations are listed with error bars. After the first few generations the energy drops, and after only eight generations the variance increases significantly. Although it is impossible to observe convergence the energy of each generation is an upper bound to the exact nonrelativistic ground state energy. For the F atom we obtain $E_0 = -99.731(4)$ Hartree for the eighth generation, and for the FH molecule we obtain $E_0 = -100.458(5)$ Hartree. Both values are upper bounds and overlap the current estimates of the nonrelativistic ground state energies of -99.734 Hartree²⁶ and -100.460 Hartree for F and FH, respectively. The latter value has been calculated from the ground state energy of the F atom and the corrected experimental dissociation energy. Unfortunately, the error bars of these calculations cannot be reduced easily as the RN-GFQMC calculations in this work are (despite the larger error bars) computationally more expensive than the fixed-node calculations. The dissociation energy obtained from RN-GFQMC, $D_e = 142(4)$ kcal mol⁻¹, is in agreement with experiment, but with a large statistical uncertainty.

We conclude that the nodal error for FH for fixed-node QMC calculations is virtually invariant with respect to bond breaking. It remains to be determined whether the same is true for other molecules. Results for other first row diatomic hydrides are encouraging.²⁵ This work clearly demonstrates that fixed-node QMC is capable of achieving high accuracy for HF efficiently, provided that the nodal hypersurface of the trial wave function is given by determinants from near HF-limit orbitals. Using released-node QMC we were able to obtain the exact nonrelativistic total energies for both F and FH within the statistical uncertainty, but achieving chemical accuracy with this method remains very demanding.

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