Ab initio computation of forces and molecular spectroscopic constants using plane waves based auxiliary field Monte Carlo with application to N_2

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Ab initio computation of forces and molecular spectroscopic constants using plane waves based auxiliary field Monte Carlo with application to N_2

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Correlated sampling within the shifted contour auxiliary field Monte Carlo method, implemented using plane waves and pseudopotentials, allows computation of electronic forces on nuclei, potential energy differences, geometric and vibrotational spectroscopic constants. This is exemplified on the N_2 molecule, where it is demonstrated that it is possible to accurately compute forces, dissociation energies, bond length parameters, and harmonic frequencies. © *2000 American Institute of Physics.* [S0021-9606(00)30726-7]

I. INTRODUCTION

Predicting properties of matter from first principles is a major challenge, perhaps the ultimate goal of theoretical chemistry. Molecular properties are usually determined by the dynamics of nuclei on the electronic groundstate potential energy surface (PES) where energy differences are of a minute magnitude relative to absolute electronic energy. This is the energy scale conundrum of quantum chemistry. Decoupling of the energy scales can be partially achieved using pseudopotentials[1–3] though electronic energy must still be computed to high precision.

Quantum Monte Carlo (QMC) methods[4] are attractive because of the combination of high accuracy and a gentle scaling of computational burden with system size.[5] The power and applicability of QMC is enhanced by using pseudopotentials.[6–11] Yet, in spite of this, the computation of forces using QMC is problematic. The singularity in the attractive electron-nuclear potential leads to an infinite variance of the QMC Hellmann–Feynman force.[12] Methods using the fixed node approximations face an additional complication of determining the dependence of the location of nodes on the nuclear configuration. An alternative to the Helmann–Feynman theory is a straightforward numerical derivative[13]

$$F_{\mathbf{x}} = \lim_{|\delta\mathbf{x}|\to 0} \frac{E(\mathbf{R}+\delta\mathbf{x}) - E(\mathbf{R})}{|\delta\mathbf{x}|},$$

where, $E(\mathbf{R})$ and $F_{\mathbf{x}}$ are, respectively, the electronic energy and the force component on an atomic nucleus at position $\mathbf{R}$. Usually, the energy estimators $E(\mathbf{R})$ and $E(\mathbf{R}+\delta\mathbf{x})$ are independent, with statistical errors (SE) σ_E. This makes the force SE, $\sqrt{2}\sigma_E/|\delta\mathbf{x}|$, formally infinite, severely limiting the ability to compute force in QMC, although impressive progress has been made over the past years[12–16] and even quite recently.[17]

This paper explores the PES, force, frequency, and spectroscopic constants computation using shifted contour auxiliary field Monte Carlo[18–21] in its plane waves pseudopotential implementation (PW-SCAFMC).[22] We develop a method for correlated sampling of electronic energy in different nuclear configurations in such a way that force computations are possible, without divergence of the variance as $\delta x \to 0$. This is clearly seen in Fig. 1, where the variance of the force on the nuclei of N_2 is shown to be largely independent of the size of δx.

We demonstrate the method on the nitrogen molecule, a popular benchmark system for high correlation methods in the past decade,[23–30] showing that it is possible to obtain high accuracies similar to methods such as coupled cluster single double (triple).[31]

Most computations were carried out on ''Cubiot'' — an 84 Pentium-III cluster, running under Red-Hat LINUX and MOSIX cluster optimization software.[32]

II. THEORETICAL METHOD

Consider the many-electron Hamiltonian $\hat{H} = h^T\hat{\rho} + \frac{1}{2}\hat{\rho}^T V\hat{\rho}$, where $\hat{\rho}$ is the electron density operator, and h and V are a column vector and a matrix describing the one body and two body terms of the electronic Hamiltonian. The ground state (GS) energy is given by

$$E_{\mathrm{GS}} = \lim_{\beta\to\infty} \frac{\langle\Phi|\hat{H}e^{-\beta\hat{H}}|\Phi\rangle}{\langle\Phi|e^{-\beta\hat{H}}|\Phi\rangle},$$

where Φ is an antisymmetric N-electron wave function not orthogonal to the GS. The rate of convergence depends on the similarity of Φ to the GS so a practical convention is to use the Hartree–Fock determinant $\Phi = \Phi_{\mathrm{HF}}$. The expression for the ground state energy can be realized computationally by means of the Stratonovich–Hubbard transformation, with Monte Carlo integration over auxiliary fields.[33] A crucial ingredient is the imaginary contour shift $\alpha(\mathbf{r})$ of Neuhauser,[19] which brings the imaginary time evolution operator to the following expression:[20]

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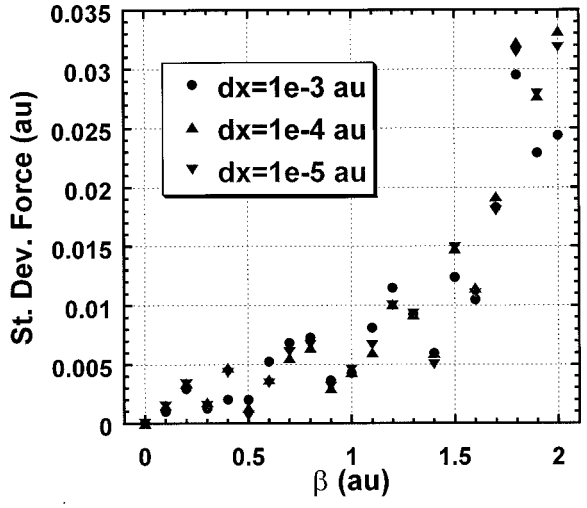

FIG. 1. The PW-SCAFMC root-variance of the force estimator is quite independent of δx (computed for N_2 in a cell size of 8 bohr at bond length of 2 bohr using 4×1000 Monte Carlo iterations).

$$e^{-\beta\hat{H}}=\exp\left(\frac{1}{2}\int_0^\beta \alpha_\tau^T V\alpha_\tau\, d\tau\right)\times\left\langle \exp\left(i\int_0^\beta \sigma_\tau^T V\alpha_\tau\, d\tau\right)U_{\sigma-ia}(\beta)\right\rangle_{W\{\sigma\}}. \quad (2.1)$$

Here, the evolution operator is a weighted average, over all time-dependent auxiliary fields $\sigma(t)$ $(0\leqslant t\leqslant\beta)$, of a one-particle evolution operator given by

$$U_{\sigma-i\alpha}(\beta)=T\exp(-\textstyle\int_0^\beta(h+iV\{\sigma(\tau)-i\alpha(\tau)\})^T\hat{\rho}\, d\tau).$$

The fields $\sigma(t)$ are sampled from a Gaussian weight $W\{\sigma\}=\exp(-\frac{1}{2}\int_0^\beta\sigma^T(\tau)V\sigma(\tau)\,d\tau)$.

A correct value of α is crucial for stabilizing the statistics. In Ref. 20 we showed that it should be equal to the exact GS density[20] $\alpha(\mathbf{r})=\langle\Psi_{GS}|\hat{\rho}(\mathbf{r})|\Psi_{GS}\rangle$, which is unknown. Thus, a suboptimal Hartree–Fock density is used. Note that the functional sampling weight of the auxiliary fields is *universal*: It depends on the electron–electron interaction and not on the location of the nuclei. This enables correlated sampling: Identical auxiliary fields are used for computing electronic energy at different nuclear configurations.

Application of the above-mentioned formalism within PW-SCAFMC is made using plane waves to represent one-electron orbitals.[34] The molecule is placed in a cubic cell of length L, periodic boundary conditions are applied, and a grid spacing δx controls the maximum wave number. Time evolution is efficiently and accurately imposed using the Kosloff–tal–Ezer method.[35] References 20 and 22 contain more details for computing electronic energy using PW-SCAFMC.

III. EXAMPLE: SPECTROSCOPIC CONSTANTS OF N_2

The method is applied to the triple bond of nitrogen. Troullier–Martins[36] local density approximation-based pseudopotentials, generated by FHI98PP[37] are used. Grid spacing was $\delta x=0.5$ bohr and two cell sizes of $L=8$ and 12 bohr were used.

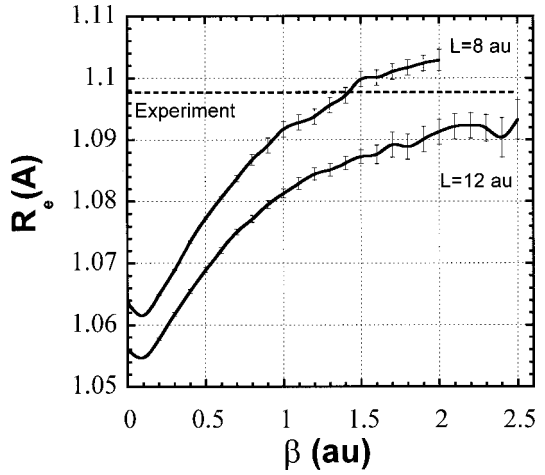

FIG. 2. Bond length parameter R_e vs β for two cell sizes. The curves are guides to the eye.

The following procedure was taken for computing spectroscopic constants. For the nuclear bond lengths $R_i=1.9$, 2.0, 2.1, 2.2, 2.3 bohr $(i=1-5)$ the correlated electronic ground energies $E_{N_2}(i,\beta)$ were determined.

For each value of β, a Morse potential curve $V(R)=D(e^{-2a(R-R_e)}-2e^{-a(R-R_e)})$ was determined via generalized least squares fit of three parameters, a, R_e, and D, to the five energy differences $D_i(\beta)=E_{N_2}(i,\beta)-2E_N(\beta)$, where $E_N(\beta)$ is the GS energy of the $N(^4\mathbf{S})$ atom, also computed using PW-SCAMFC. The atomic and molecular energies were not computed in correlated manner.

The harmonic frequency parameter is deduced from the Morse potential parameters D, a, and μ, where, $\mu=14.003\,06$ u is the atomic mass[38] of nitrogen. Results for these constants are shown in Figs. 2, 3 and 4. Parameter values for final inverse temperatures of $\beta_f=2$ a.u. are summarized in Table I. 50 000 iterations were performed for

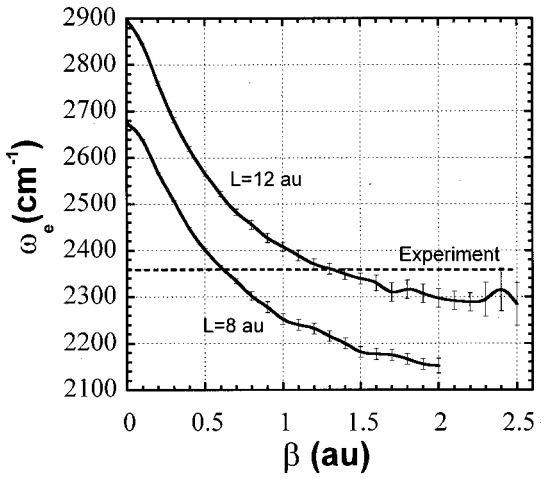

FIG. 3. The harmonic frequency ω_e as a function of inverse temperature β for two cell sizes. The curves are guides to the eye.

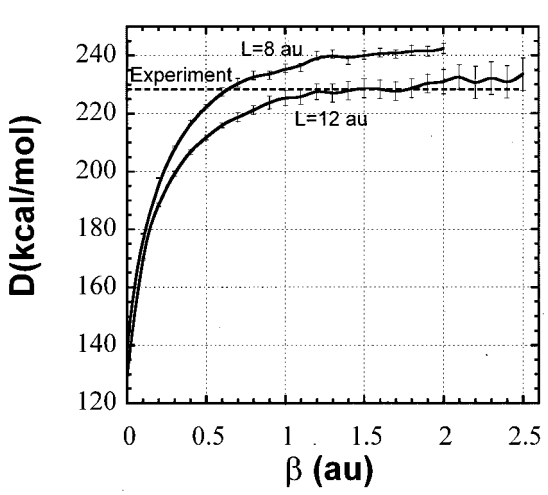

FIG. 4. The bond energy parameter D as a function of inverse temperature β for the two cell sizes. The curves are guides to the eye.

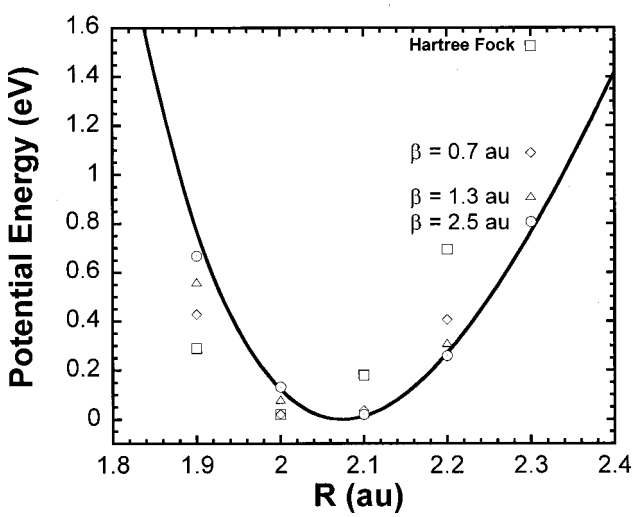

FIG. 5. Convergence of PES with increasing β. The solid line is a cubic spline through *ab initio* energy differences of Ref. 28 (the zero of energy is taken as the minimum). Statistical errors in correlated energy differences at the largest β are ± 0.03 eV (note that the statistical errors of absolute energy are ± 0.18 eV).

these calculations. The iterations were divided into four bins of 10 000 iterations. This allows estimation of statistical errors by standard deviation.

The smaller cell size leads to overestimated bond-energy and length parameters and underestimated harmonic frequency. Discrepancies are considerably smaller for the larger cell size. To estimate the cell size effect, we studied the Hartree–Fock infinite cell-size limit, and found a bond length decrease of 0.002 Å, a bond energy decrease by 0.7 kcal/mol, and a harmonic frequency *increase* by 45 cm^{-1}.

The statistical errors of the dissociation energies are large due to the fact the atomic and molecular energies are statistically uncorrelated. When energetic differences are studied, the advantage of the correlated sampling is evident. In Fig. 5, the computed potential energy surface (PES) is studied in comparison to the *ab initio* results of Gdanitz.[28] Because only energetic differences are important, the statistical errors are 0.03 eV at the largest β. Interestingly, it seems the small bond length energy is more sensitive to the finite cell size than larger bond length, so most of the error in our computation is due to the smallest bond length point.

IV. SUMMARY

A new *ab initio* method for computing molecular properties and PES was presented. The method fully correlates valence electrons without fixed-node approximations. Correlated sampling facilitates the computation of the electronic forces. The method was tested on the nitrogen triple bond. We did not fully converge results with respect to increasing cell size, although, by examining this effect within the Hartree–Fock regime, we estimate that the bond energy and bond length will slightly decrease, while harmonic frequency will grow by about 45 cm^{-1}. The remaining discrepancies between our computation and experiment should be attributed to the use of pseudopotentials.

This work takes an additional step in establishing auxiliary field Monte Carlo as a useful accurate method for electronic structure. Future developments are needed for avoiding the need to take large β limit.

TABLE I. Computed and experimental spectroscopic constants of N_2. Computation results are at largest β computed for the two cell sizes. $\delta x = 0.5$ bohr. Numbers in parentheses are magnitude of statistical error.

	$L=8$ a.u.	$L=12$ a.u.	Experiment
D (kcal/mol)	240(5)	233(6)	228.4
$R_e(\beta_f)$ (Å)	1.103(2)	1.093(3)	1.0977
$\omega_e(\beta_f)$ (cm^{-1})	2150(15)	2285(45)	2358.57

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