

Quantum Monte Carlo of Nitrogen: Atom, Dimer, Atomic, and Molecular Solids

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We have carried out variational and fixed-node diffusion Monte Carlo calculations for nitrogen in atomic, molecular, and compressed solid forms. This is the first work which treats the electron correlation in nitrogen solids with accuracy comparable to the most exact results on the atom and molecule. Comparison with local density approximation (LDA) calculations reveals LDA total energy errors varying from 2.1 eV in the atom to 0.7 eV/atom in the solid. We have also calculated the electronic energy gap for the compressed solid and compared it with the LDA (30% lower) and Hartree-Fock (100% higher) estimations.

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The nitrogen dimer is known as a very stable triple-bond molecule with an extremely small interatomic distance. The strong molecular bond persists in condensed forms of nitrogen which are molecular solids and liquids at ordinary pressures. Nevertheless, a number of theoretical calculations have predicted that nitrogen will transform to a nonmolecular solid by application of pressure well within the range of current experimental capabilities [1-3]. Very recently, a new covalent structure has been proposed [3] as a possible high-pressure solid phase of atomic nitrogen. To date, however, experimental studies [4] have not found the predicted transition.

So far electronic structure calculations of nitrogen solids have relied on the commonly used local density approximation (LDA) [1-3,5]. However, because of the competition between multiple molecular bonds and other types of bonding, correlation effects are expected to be especially significant in these systems. One of the important issues we address in this Letter is the accuracy of the LDA in such cases, which we quantify by carrying out nearly exact quantum Monte Carlo [6-9] calculations of the correlation energies. Also, in order to shed light on the excitation spectrum of the most likely candidate for the atomic structure of nitrogen [3], we have performed the calculation of an excited electronic state which we compare with LDA and Hartree-Fock (HF) estimations. To our knowledge, this is the first quantum Monte Carlo gap estimation for solids.

The present work demonstrates wide applicability and further development of the quantum Monte Carlo approach. We start with the valence-only Hamiltonian with core states eliminated by *ab initio* nonlocal pseudopotentials because the core electrons are difficult to treat with Monte Carlo methods [6,7]. In the next step an optimized correlated trial function is employed using variational Monte Carlo (VMC), and, finally, most of the variational bias is removed by the stochastic solution of the Schrödinger equation using the diffusion Monte Carlo (DMC) method. A detailed description of the VMC and DMC methods can be found elsewhere [8,9] and we give

only the main points. The VMC energy is estimated by a Monte Carlo evaluation of the integral

$$E = \frac{\int |\Psi(R)|^2 [H\Psi(R)/\Psi(R)] dR}{\int |\Psi(R)|^2 dR}, \quad (1)$$

where H is a Hamiltonian, $\Psi(R)$ is a trial function, and the integration is over the configuration space of electrons. The DMC method simulates stochastically the imaginary time Schrödinger equation

$$f(R, t + \tau) = \int G(R, R', \tau) f(R', t) dR', \quad (2)$$

where the importance sampling by $\Psi(R)$ is invoked so that $f(R, t) = \Psi(R)\Phi(R, t)$ while $G(R, R', \tau)$ is the corresponding propagator known in an analytic form for $\tau \rightarrow 0$ [8,9]. The lowest energy solution $\Phi(R, t)$ with fermion nodes prescribed by $\Psi(R)$ (fixed-node approximation [8,10]) is found by iterating (2) to large t .

In general, the trial function is a linear combination of spin-up and -down Slater determinant products multiplied by a correlation factor [11]

$$\Psi(R) = \sum_n e_n D_n^\uparrow D_n^\downarrow \exp \left[\sum_{I, I' < j} u(r_{Ii}, r_{Jj}, r_{ij}) \right], \quad (3)$$

where I denotes ions, i, j label electrons, and r_{Ii}, r_{Jj}, r_{ij} are corresponding distances. The Slater determinants were built from the HF orbitals using a localized basis set (Gaussian or numerical). The HF equations were solved by GAUSSIAN92 [12] and GAMESS [13] packages for atom and molecule, and by CRYSTAL92 [14] for solids. In atomic and molecular calculations the function $u(r_{Ii}, r_{Jj}, r_{ij})$ is the same as in our previous studies [15] and includes 21 variational parameters which are optimized within the VMC method [11]. For solids $u(\dots)$ is independent of r_{Ii}, r_{Jj} , or r_{ij} whenever r_{Ii}, r_{Jj} , or r_{ij} is larger than half of the simulation cell edge, respectively, and the number of variational parameters is 6. The development of an efficient functional form of the correlation factor for solids is still in progress and further computational details will be published elsewhere [16].

The core electrons were eliminated from calculations

TABLE I. The valence total and correlation energies (a.u./atom) for the nitrogen atom, dimer, molecular $Pa3$, and atomic $I2_3$ solid structures found by the Hartree-Fock (HF) and variational and diffusion Monte Carlo (VMC and DMC). TM and PC refer to Troullier and Martins [21] and Pacios and Christiansen [22] pseudopotentials, respectively. All other calculations have been done with pseudopotentials of Stevens, Basch, and Krauss [20].

	HF	VMC	DMC	$E_{\text{cor}}^{\text{DMC}}$
Atom (TM)	-9.6741	-9.7841(6)	-9.7944(6)	0.120(1)
Atom (PC)	-9.6501	-9.7616(8)	-9.7715(9)	0.121(1)
Atom	-9.6441	-9.7558(8)	-9.7649(5)	0.121(1)
Dimer	-9.7401	-9.922(1)	-9.944(1)	0.205(1)
$Pa3$	-9.6443	-9.830(2)	-9.887(3)	0.244(3)
$I2_3$	-9.6531	-9.834(1)	-9.889(3)	0.236(3)

by *ab initio* nonlocal pseudopotentials. The difficulties with the nonlocal operator in the DMC method were overcome by the technique of evaluating pseudopotentials with the trial function [17] which we applied and tested on several systems earlier [15,18]. Additional checks have shown that the impact of this approximation on the energy was rather small because of a short radial range of nitrogen pseudopotentials. Trial functions with various degrees of correlation used for nonlocal pseudopotential evaluation resulted in systematic energy shifts within ≈ 0.1 eV/atom. Similar behavior was observed in the Fe atom simulations using short-ranged Ne-core pseudopotentials [19] while stronger impact was found for much more extended Ar-core pseudopotentials [15].

The calculated total energies for the nitrogen atom, dimer, and solids are listed in Table I while the energy differences are in Table II (statistical errors are in parentheses). Most of the calculations have been done with the HF *ab initio* norm-conserving pseudopotentials of Stevens, Basch, and Krauss [20]. For a comparison, Table I also includes atomic calculations with LDA "soft" pseudopotentials of Troullier and Martins [21] and with another HF pseudopotential by Pacios and Christiansen [22]. Moreover, we have carried out an independent test of the N atom by a large configuration interaction calculation which agrees with the DMC energy within 0.05 eV.

Because of large correlation energy, the N_2 molecule is an excellent test case for a correlated method. The VMC calculation of the N_2 ground state $^1\Sigma_g$ at equilibrium bond length has obtained a remarkable 88(1)% of the correlation energy, to our knowledge the best VMC result for such a molecule [23]. The DMC then gives 98(1)% of the experimental binding energy, which is comparable with the accuracy of the most extensive quantum chemistry calculations [24]. The remaining difference with experiment, we believe, is caused mainly by the fixed-node error.

The calculations for the solid molecular ($Pa3$) and

TABLE II. The binding energies (eV/atom) of the nitrogen dimer and two compressed solid systems. The LDA results are from Ref. [3] which used Troullier-Martins pseudopotentials (reference atomic energy of -9.7191 a.u. from LDA with spin density correction). The experimental value is corrected for a zero point energy [23].

	HF	LDA	VMC	DMC	Expt.
Dimer	2.61	5.85	4.52(3)	4.87(3)	4.96
$Pa3$	0.01	4.45	2.0(1)	3.3(1)	...
$I2_3$	0.25	4.75	2.1(1)	3.4(1)	...

atomic ($I2_3$) cubic structures were carried out in periodic boundary conditions with eight atoms in the simulation cell which corresponds to the Brillouin zone occupation by one k point in the former and two k points in the latter case. Both systems were compressed to the density 0.15 atom/ \AA^3 which was found by LDA [3] to give the energy minimum of the $I2_3$ structure. The Monte Carlo energies of $Pa3$ and $I2_3$ structures were corrected for finite size effects by additive corrections -0.36 and 0.08 eV/atom, respectively. Each of these corrections was evaluated as the difference between the fully converged LDA energy and LDA energy calculated with k -point occupation identical to that used in the Monte Carlo calculation. The corrected VMC and DMC energies are in Table I. A Gaussian basis set $6s6p1d$ was used for the solid state calculations. The d orbital is important and lowers the energy by 0.69 and 0.25 eV/atom in HF and DMC calculations, respectively.

The comparison of DMC total energies with recent LDA calculations in Fig. 1 clearly illustrates the improvement of LDA total energy with increasing "homogeneity" (atom \rightarrow dimer \rightarrow molecular solid \rightarrow atomic solid) and with increasing electronic density. The difference in the two solids is due to different correlations in the molecular and the nonmolecular forms. Eventually, by extrapola-

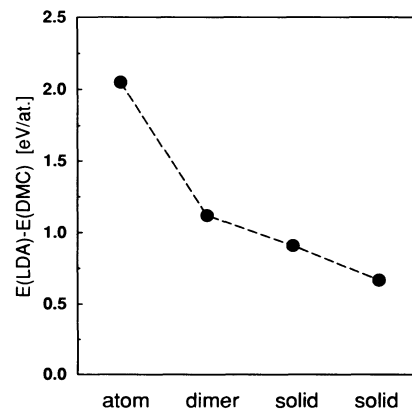


FIG. 1. The difference in the total energy from LDA [3] and DMC calculations for the nitrogen atom, dimer, and two types of solids ($Pa3$ and $I2_3$).

tion to the homogeneous electron gas case, the LDA energy will become identical to the DMC result since the LDA exchange correlation was fit with the DMC calculations of this system [25].

The final point of our effort was to estimate the energy of an excited electronic state in the solid and thus open a road towards high accuracy *ab initio* estimations of band gaps. Usually, the LDA eigenvalues interpreted as excited state bands give gaps 30%–50% smaller than experiment; in some cases, like transition metal oxides, the errors are even larger.

There are several complications related to the calculations of excited states. An excited state which is not the ground state of a given symmetry is much more difficult to calculate by the DMC method [26]. However, excited states belonging to a different symmetry class than the ground state can be treated directly because the solution of Eq. (2) will converge to the lowest state of the given symmetry. Since the translational symmetry of states in the crystal is labeled by occupation numbers in \mathbf{k} space, we use the DMC method directly for an excitation of an electron from the state \mathbf{k}_g to a different crystal momentum \mathbf{k}_e , e.g., as in an indirect gap. The finite size of the system is another complication. The excitation $\mathbf{k}_g \rightarrow \mathbf{k}_e$ creates an exciton (electron-hole pair) with a localization length given by the size of the simulation cell. Consequently, the excitation energy is smaller than the exciton interaction energy. While for a small simulation cell the exciton localization is artificially small, with increasing cell size the exciton will stabilize at the equilibrium size which minimizes the total energy. Thus our calculations should be comparable to an exciton energy. LDA and HF calculations do not include exciton effects, and hence the comparison must include an estimate of the size of such effects. Fortunately, exciton binding energies in comparable covalent solids are much smaller than the excitation energy which we find here.

The excited state trial function deserves some attention. If one electron is excited in a single determinant, the wave function has a spin contamination. Although the consequences are expected to be weak in the present case of a large gap nonmagnetic insulator, it is possible to avoid this problem by using a proper spin singlet which is a superposition of the two determinant products in (3). This was done in the present study.

The HF band structure of the atomic solid in the $I2_13$ structure (bcc with four atoms per primitive cell) is shown in Fig. 2. The LDA valence bands are narrower but otherwise very similar to the HF valence bands, while the LDA conduction states lie much lower than their HF counterparts [27]. The states occupied in our simulation are denoted by the filled circles. We excited the electron from the highest occupied Γ state to the lowest unoccupied H state. The $\Gamma \rightarrow H$ gap is 6.1 eV from LDA and 18.0 eV from Hartree-Fock calculation. The Monte Carlo calculations lead to the corresponding exciton energy (the excitation-exciton interaction), which is found to be

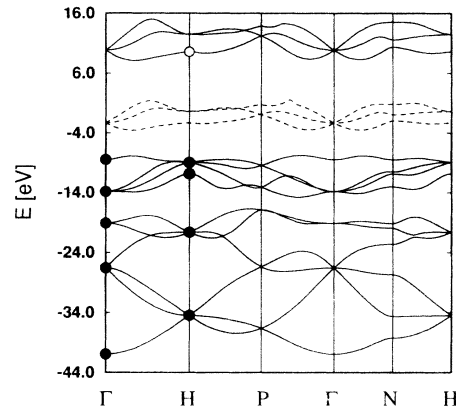


FIG. 2. The band structure of the atomic nitrogen solid in the $I2_13$ structure from Hartree-Fock calculations. Three LDA conduction bands (dashed lines) are inserted using the highest HF occupied band as a reference level. The filled circles denote states occupied in the simulation. The excited state was created by promoting the electron from the highest occupied Γ state to the lowest unoccupied H state (unfilled circle).

8.3(3) eV from the VMC method and 8.1(3) eV from the more exact DMC method. For a Mott-Wannier exciton the energy gain (in a.u. units) from the electron-hole interaction can be expressed as $E_{e-h} = \frac{1}{2} \epsilon r_{loc}$, where ϵ is the static dielectric constant and r_{loc} is the localization length. In our case we have an artificial confinement, so that r_{loc} corresponds to the side of the simulation cell. With $\epsilon \approx 5$ we estimate that the exciton interaction is ≈ 0.4 eV. Adding this value to the calculated DMC exciton energy gives our estimate for the $\Gamma \rightarrow H$ band gap of 8.5(4) eV, where the increased error bar reflects an additional uncertainty from the exciton. The LDA underestimation and HF overestimation of the excitation energy is in accord with error trends observed in similar cases [27].

In conclusion, our calculations quantify the effects of correlation upon total and binding energies in nitrogen systems with very different electronic structures. Comparison with local density calculations shows that there are varying errors in the total energy for atom, dimer, and solids. In addition, we have found the energy of an electronic excitation which greatly improves the results of local density or Hartree-Fock approximations. The calculations also demonstrate a significant enhancement of the quantum Monte Carlo method using pseudopotentials together with the high accuracy DMC algorithm which removes the variational bias (clearly present in our variational calculations). We believe the approach used here is a viable strategy for attacking even more demanding cases like transition metal oxides, where accurate description of exchange and correlation is the key issue.

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- [1] A. K. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985); A. K. McMahan, Physica (Amsterdam) **139 & 140B**, 31 (1986).
- [2] R. M. Martin and R. J. Needs, Phys. Rev. B **34**, 5082 (1986).
- [3] C. Mailhiet, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14419 (1992).
- [4] R. Reichlin, D. Schiferl, S. Martin, C. Vanderborgh, and R. L. Mills, Phys. Rev. Lett. **55**, 1464 (1985); P. M. Bell, H. K. Mao, and R. J. Hemley, Physica (Amsterdam) **139 & 140B**, 16 (1986); H. Lorenzana (private communication).
- [5] S. P. Lewis and M. L. Cohen, Phys. Rev. B **46**, 11117 (1992).
- [6] F. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. Lett. **61**, 1631 (1988); Phys. Rev. B **42**, 3503 (1990).
- [7] X.-P. Li, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **44**, 10929 (1991); G. B. Bachelet, D. M. Ceperley, and M. G. B. Chiochetti, Phys. Rev. Lett. **62**, 2088 (1989).
- [8] W. A. Lester, Jr. and B. L. Hammond, Annu. Rev. Phys. Chem. **41**, 283 (1990); P. J. Reynolds, D. M. Ceperley, B. J. Alder, and W. A. Lester, J. Chem. Phys. **77**, 5593 (1982).
- [9] D. M. Ceperley and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979); K. E. Schmidt and M. H. Kalos, in *Monte Carlo Methods in Statistical Physics II*, edited by K. Binder (Springer, Berlin, 1984).
- [10] J. B. Anderson, J. Chem. Phys. **63**, 1499 (1975); **80**, 2675 (1984).
- [11] C. J. Umrigar, K. G. Wilson, and J. W. Wilkins, Phys. Rev. Lett. **60**, 1719 (1988); K. E. Schmidt and J. W. Moskowitz, J. Chem. Phys. **93**, 4172 (1990).
- [12] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, computer code GAUSSIAN92, Rev. B, Gaussian, Inc., Pittsburgh, PA, 1992.
- [13] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, S. J. Su, T. L. Windus, and S. T. Elbert, computer code GAMESS, QCPE Bulletin **10**, 52 (1990).
- [14] C. Pisani, R. Dovesi, and C. Roetti, *Hartree-Fock $\bar{A}b \bar{I}n \bar{I}t$ io Treatment of Crystalline Systems* (Springer, Berlin, 1988); R. Dovesi, V. R. Saunders, and C. Roetti, CRYSTAL92: An *Ab Initio* Hartree-Fock LCAO Program for Periodic Systems, User Manual, Università di Torino and SERC Daresbury Laboratory, 1992.
- [15] L. Mitáš, in *Computer Simulation Studies in Condensed Matter Physics V*, edited by D. P. Landau, K. K. Mon, and H. B. Schüttler (Springer, Berlin, 1993), p. 94.
- [16] L. Mitáš (to be published).
- [17] M. M. Hurley and P. A. Christiansen, J. Chem. Phys. **86**, 1069 (1987); B. L. Hammond, P. J. Reynolds, and W. A. Lester, Jr., *ibid.* **87**, 1130 (1987).
- [18] L. Mitáš, E. L. Shirley, and D. M. Ceperley, J. Chem. Phys. **95**, 3467 (1991).
- [19] L. Mitáš, Phys. Rev. A (to be published).
- [20] W. J. Stevens, H. Basch, and M. Krauss, J. Chem. Phys. **81**, Pt. II, 6026 (1984).
- [21] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
- [22] L. F. Pacios and P. A. Christiansen, J. Chem. Phys. **82**, 2664 (1985).
- [23] R. P. Subramaniam, M. A. Lee, K. E. Schmidt, and J. W. Moskowitz, J. Chem. Phys. **97**, 2600 (1992).
- [24] J. Almlöf, B. J. DeLeeuw, P. R. Taylor, C. W. Bauschlicher, Jr., and E. M. Siegbahn, Int. J. Quantum Chem. Symp. **23**, 345 (1989).
- [25] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [26] D. M. Ceperley and B. Bernu, J. Chem. Phys. **89**, 6316 (1988).
- [27] S. Massidda, M. Posternak, and A. Baldereschi, Phys. Rev. B **48**, 5058 (1993).