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Exploration of Brueckner orbital trial wave functions in diffusion Monte Carlo calculations

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ABSTRACT

This study explores the utility of Brueckner orbitals as trial wave functions for diffusion Monte Carlo (DMC) calculations. Comparison is made with Hartree–Fock (HF) and density functional theory (DFT) orbitals allowing for an assessment of how well the three sets of orbitals describe the nodal surfaces. For the neutral test systems, PBE0 orbitals or Brueckner orbitals give DMC energies that are appreciably lower than those obtained using Hartree–Fock orbitals. For a CO_2^- anion test case, a significantly lower DMC energy is obtained when using Brueckner orbitals rather than DFT orbitals as the trial function.

1. Introduction

The diffusion Monte Carlo (DMC) [1,2] method is capable of giving exact electronic energies within the fixed-node approximation [3,4]. A trial wave function, generally taken to be a Slater determinant of orbitals from density-functional theory (DFT) or Hartree–Fock (HF) calculations, is used to enforce the fixed-node approximation. This condition is required to prevent the ground state wave function from collapsing to a Bosonic state. If the trial wave function were to exactly describe the nodal surface for exchange of electrons, the DMC method, if used in all-electron calculations and run for sufficiently large number of moves and corrected for time step bias, would give the exact non-relativistic ground state energy [5]. In general, trial functions employing a Slater determinant of DFT orbitals give lower total energies than do trial functions employing a Slater determinant of Hartree–Fock orbitals, which implies that the use of DFT orbitals provides a better description of the nodal surface [6,7]. In the present study, we explore the use of trial functions comprised of a Slater determinant of Brueckner orbitals (BO) [8,9]. One might expect that such trial wave functions would give a nodal surfaces superior to a Slater determinant of DFT orbitals, as the Slater determinant of BOs is that with the maximum overlap with the exact wave function for the basis set employed [10].

There has been considerable discussion in the literature concerning the similarity and differences between HF, DFT, and Brueckner orbitals. Scuseria [11] has shown that the DFT equations can be derived through approximations made to the Brueckner equations. Lindgren and Salmonson [12] have argued that DFT and Brueckner orbitals are closely related. Heßelmann and Jansen have shown that Brueckner orbitals offer an improvement over Hartree–Fock orbitals when calculating first-order intermolecular interaction energies [13], whereas DFT orbitals may or may not give an improved description of the first-order Coulomb and exchange energies, with the performance depending on the functional used to generate the orbitals [14]. Jankowsi et al. [15,16] calculated the distance between orbital subspaces, and based on this measure, concluded that DFT orbitals can differ appreciably from both HF and Brueckner orbitals. An alternative criterion for testing the quality of various types of orbitals is to determine how well they describe the nodal surface for exchange of electrons which can be evaluated by assessing their performance when used as trial functions for DMC calculations. In this study, we investigate the performance of trial functions using HF, DFT, and Brueckner orbitals in DMC calculations on a series of diatomic molecules and on a bent CO_2^- ion to determine whether the use of Brueckner orbitals leads to lower DMC energies than obtained using trial functions comprised of DFT orbitals.

2. Methodology

The diatomic molecules studied include BeO [17], N_2 [18], O_2 [18], F_2 [18], and CN [18], with the equilibrium geometries being taken from the respective references. To obtain atomization energies, calculations were also carried out on the atoms in their ground electronic states. For these test systems, both pseudopotential and all-electron calculations were carried out. In the all-electron calculations the orbitals were expanded in terms of the cc-pVTZ basis

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set [19]. In the calculations of the dimer atomization energies using pseudopotentials, the Trail-Needs AREP pseuduopotentials [20,21] and basis sets of Xu et al. [22] were used for all atoms with the exception of Be. For N, F, and C, the *spd* portions of the triple-zeta basis set were used and for oxygen the *sp* portion of the quintuple basis set was combined with the *d* functions from the triple-zeta basis set. For Be, the pseudopotential and valence triple-zeta basis set of Burkatzki, Filippi, and Dolg (BFD) were used [23]. The calculations on CO_2 and its anion made use of the Trail-Needs pseudopotentials [20,21]. For both C and O 8*s*8*p*3*d* contracted Gaussian basis sets formed by adding to the 6*s*6*p* portion of the quintuple-zeta basis set of Xu et al. [22] two diffuse *s* and two diffuse *p* functions with exponents three and nine times smaller than those of the most diffuse primitive functions in the 6*s*6*p* set as well as *d* functions with exponents of 0.5586, 0.2271, and 0.1024 and 1.2192, 0.4904, and 0.2053 for carbon and oxygen atoms, respectively. The hybrid B3LYP [24,25] functional was used for the DFT calculations on the all-electron systems, and both the B3LYP and PBE0 [26] functionals were used for the pseudopotential calculations of the diatomics. The Brueckner orbitals were obtained from coupled-cluster calculations in which the orbitals were rotated so as to eliminate single excitations to all orders [27,28]. For one system, N_2, we also considered a trial function based on PBE [29] orbitals and also employed the more flexible cc-pVQZ-*g* basis set for the all-electron calculations [19]. In addition to the diatomic test cases described above, we also considered CO_2 and $CO_2{}^-$ with CO bond lengths of 1.215 Å and an OCO angle of 147°. This geometry was chosen because earlier studies have shown electron correlation effects are important for the vertical electron detachment energy (VDE) which increases from 0.18 to 0.32 eV in going from the Hartree–Fock to CCSD(T) method [30]. DFT methods, on the other hand, drastically overbind the excess electron at this geometry, with, for example, the B3LYP value of the VDE being 0.80 eV. All open-shell systems were described using spin-unrestricted orbitals. The trial functions were generated using the GAUSSIAN 09 code [31], and the diffusion Monte Carlo calculations were carried out using the CASINO code [32].

The correction scheme of Ma et al. [33] was used in the DMC calculations to account for electron-nuclear cusps in the all-electron calculations. The DMC calculations were preceded by variational Monte Carlo (VMC) calculations to optimize (*via* energy minimization) the parameters in the Jastrow factors [34] which include explicit electron-nuclear (*e-n*), electron–electron (*e–e*), and *e-e-n* terms. The all-electron DMC calculations were carried out for time steps of 0.001, 0.003, 0.005, and 0.007 a.u., and the resulting energies were extrapolated to zero time step by use of quadratic fits. The calculations were carried out with 40 000 walkers and for sufficient number of steps so as to reduce the statistical errors in the extrapolated DMC energies of the diatomics and their atomization energies to under 0.3 and 0.5 kcal/mol, respectively. The errors in the atomization energies are defined as the differences between the experimental values, corrected for vibrational zero-point energy (ZPE), and the corresponding DMC results. For N_2, O_2, F_2, and CN, the experimental atomization energy values and zero-point energies are taken from reference [35]. For BeO, the experimental atomization energy and ZPE are taken from cccbdb.nist.gov.

The parameters of the Jastrow factors for the diatomics with pseudopotntials and for the CO_2 test system were optimized *via* variance minimization. Time steps of 0.005, 0.0075, and 0.01 a.u. were used in the DMC calculations on the diatomic species with pseudopotentials, and time steps of 0.0125, 0.003, and 0.005 a.u. were used for the CO_2 test system. Linear fits were used to extrapolate to zero time step. The T-move procedure was used in the pseudopotential calculations to correct for the localization error [36].

3. Results

The total energies from the all-electron DMC calculations on the diatomic species and associated atoms are summarized in Table 1. For the atoms, DMC calculations with the Hartree–Fock, B3LYP, and Brueckner orbitals give total energies that essentially agree to within statistical error. This is consistent with earlier studies [7] that found that for atoms DMC energies were largely insensitive to whether DFT or HF orbitals are used for the trial functions. The situation is quite different for the diatomics: going from HF orbitals to B3LYP orbitals leads to energy decreases ranging from 1.63 kcal/mol for BeO to 13.8 kcal/mol for CN. The DMC energies obtained using B3LYP and Brueckner orbitals agree to within one standard deviation for N_2 and BeO, but for O_2, F_2, and CN, significantly lower DMC energies are obtained when using B3LYP orbitals in the trial function. It should be noted that the use of spin-unrestricted calculations introduces spin contamination in the wave function. This has a larger effect on the Hartree–Fock orbitals than it does for the B3LYP and Bruckner orbitals. The largest spin contamination is found for the CN molecule, which has S^2 expectation values of 1.158, 0.758, and 0.764 for the HF, B3LYP, and Brueckner orbital wave functions, respectively, compared to the exact value of 0.750. While using RHF rather than UHF orbitals can result in lower DMC energies for open-shell systems [7,37] it would not change the qualitative result that lower DMC energies result when using B3LYP and Brueckner orbitals than when using HF orbitals (whether RHF or UHF), and that use of B3LYP orbitals generally give a lower DMC energy, thus superior nodal surface, than use of Brueckner orbitals. Our DMC calculations using Hartree–Fock

Table 1
Total energies from DMC calculations[a] using Hartree–Fock, B3LYP, and Bruckner orbitals.

Species	Energy[b] (a.u.)			
	Hartree–Fock	B3LYP	Brueckner	Brueckner (cc)[c]
Beryllium	−14.6575(1)	−14.6572(1)	−14.6575(1)	–
Carbon	−37.8296(2)	−37.8301(2)	−37.8296(2)	–
Nitrogen	−54.5759(2)	−54.5765(2)	−54.5757(2)	–
Oxygen	−75.0512(2)	−75.0518(2)	−75.0518(3)	–
Fluorine	−99.7161(3)	−99.7169(3)	−99.7161(3)	−99.7163(2)
N_2	−109.5007(6)	−109.5047(4)	−109.5042(4)	–
O_2	−150.2808(5)	−150.2873(5)	−150.2856(5)	–
F_2	−199.4740(5)	−199.4850(2)	−199.4812(5)	−199.4816(3)
BeO	−89.8823(4)	−89.8849(3)	−89.8845(3)	–
CN	−92.6668(5)	−92.6888(5)	−92.6876(5)	–

[a] Results extrapolated to d*t* = 0 as described in the text.

[b] Statistical errors (one standard deviation) are given in parentheses.

[c] Results obtained using Brueckner orbitals obtained from coupled cluster calculations including core correlation.