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Citation: The Journal of Chemical Physics **112**, 1679 (2000);
View online: https://doi.org/10.1063/1.480733
View Table of Contents: http://aip.scitation.org/toc/jcp/112/4
Published by the American Institute of Physics

JOURNAL OF CHEMICAL PHYSICS VOLUME 112, NUMBER 4 22 JANUARY 2000

Molecular electronic structure using auxiliary field Monte Carlo, plane-waves, and pseudopotentials

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(Received 27 July 1999; accepted 26 October 1999)

Shifted contour auxiliary field Monte Carlo is implemented for molecular electronic structure using a plane-waves basis and norm conserving pseudopotentials. The merits of the method are studied by computing atomization energies of H_2, BeH_2, and Be_2. By comparing with high correlation methods, DFT-based norm conserving pseudopotentials are evaluated for performance in fully correlated molecular computations. Pseudopotentials based on generalized gradient approximation lead to consistently better atomization energies than those based on the local density approximation, and we find there is room for designing pseudopotentials better suited for full valence correlation. © *2000 American Institute of Physics.* [S0021-9606(00)30304-X]

I. INTRODUCTION

Pseudopotentials[1,2] combined with quantum Monte Carlo (QMC) electronic structure methods,[3–5] such as variational[6] (VMC) or diffusion[7–12] (DMC) Monte Carlo, form a new powerful approach to quantum chemistry.[13–17] For example, with this blend of techniques it is possible to determine the stable structures of large carbon and silicon clusters.[18–20] The motivation for using pseudopotentials is practical. It reduces the number of electrons, decreases the span of energy scales (allowing larger time steps) and easily incorporates relativistic effects. Furthermore, core polarization potentials (CPP)[21,22] can account for effects of core-core and core-valence correlation.[23]

Quantum Monte Carlo methods have a definite advantage over traditional counterparts of quantum chemistry explicitly dealing with electron correlation.[24] Memory usage is small, CPU time scales gently with system size[20,25] and the algorithms are usually embarrassingly trivial to parallelize. While generally successful, present QMC approaches have limitations in terms of accuracy and scope[26–29] leaving room for new approaches to be developed. Auxiliary field Monte Carlo[30,31] (AFMC) is such a viable alternative. Historically, the method was impractical for electronic structure computations because of large statistical fluctuations caused by a numerical sign problem. Recently progress was made in this respect and it was shown[32,33] that by a specific shift of the functional integration contour into the complex plane, AFMC can be stabilized, making it applicable for molecular electronic structure computation. The power of the new method, dubbed shifted contour auxiliary field Monte Carlo (SC-AFMC), was demonstrated for some molecular systems using a Gaussian basis set.[34] Another method of stabilizing SC-AFMC within a fixed node approximation was recently developed,[35,36] although we are not aware of any applications to molecular electronic structure.

This article further establishes the validity and utility of SC-AFMC by developing a version based on plane-waves[37] and norm conserving pseudopotentials.[38] We apply the method to compute the atomization energies of small molecules.

Can we efficiently use plane-waves for accurate computation of molecular electronic structure? Plane-waves are not a natural choice for this feat. Traditionally, they were used in conjunction with density-functional theory (DFT) and served to study the electronic structure of periodic systems such as crystalline solids.[37] However, plane-waves are also useful for treating nonperiodic systems such as impurities, dislocations, surfaces, and even gas-phase molecules.[39,40] Indeed, plane-waves offer formal advantages over a localized Gaussian basis, commonly used in quantum chemistry. They are orthogonal, thus avoiding stability problems. They are homogeneous, evading Pulay terms in force computations. Unlike Gaussian basis sets, a computation using plane waves is converged by a well-defined procedure where exactly two limits need to be taken. The grid spacing must contract to zero $\delta x \rightarrow 0$ and the cubic super-cell length must extend to infinity $L \rightarrow \infty$. In general, the Hartree–Fock self-consistent field (HF-SCF) energy converges more slowly with cell size than the correlation energy. Thus, the computation of HF-SCF energy is performed in large super cells, but the correlation energy can be computed using SC-AFMC in smaller cells.

Plane-waves are inefficient for describing high kinetic-energy components in orbitals. For efficient use of the plane-waves basis, core orbitals must be eliminated and valence orbitals must be smoothed in the core region. This is the role of the *soft pseudopotentials*.[1] In conventional quantum chemistry, effective core potentials[2] are used for eliminating the core electrons and orbitals. Soft pseudopotentials do the

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same but have an additional role: They are carefully constructed to produce valence orbitals that are smooth in the core region. When using plane waves, even the hydrogen atom is described by a soft pseudopotential.

Are norm-conserving pseudopotentials useful for explicitly correlated electron computations?[41] These pseudopotentials are constructed from local density approximation (LDA) (LDA-PP) or generalized gradients approximation (GGA-PP) treatments of the atomic core. This question is addressed by comparing results based on pseudopotentials with other *ab initio* methods and experiment. We find that the LDA based pseudopotentials lead to larger errors than those based on GGA and the latter too are not ideal, leading for example to discrepancy of 0.2 eV in the atomization energy of BeH_2.

For studying the above posed questions, we treat here several small hydrogen and beryllium systems and examine the level of accuracy that can be reached. The greatest challenge is to compute the atomization energy of the beryllium dimer. This small molecule with only four valence electrons has proved over the years quite a challenge for many quantum-chemical methods, although recent attempts have been successful.[42–46] The reason for the difficulty is the small $2s$-$2p$ difference in beryllium, which induces a strong multireference character in the ground-state electronic wave function.[45,46]

The computational resources available for this work were 4 Alpha TL4100/EV56 (600 MHz) processors, two SGI Origin 2000 187 MhZ processors, and a 30 Pentium-Pro MOSIX cluster.[47] The quantum Monte Carlo programs were parallelized using the parallel virtual machine (PVM) library.

In the following, we present the HF-SCF methodology and calculation results in Sec. II. In Sec. III results for valence correlation energies are presented, followed by a summary and discussion given in Sec. IV.

II. HARTREE–FOCK ENERGY

The electronic energy of the isolated molecule is computed under the assumption of the molecule being fixed in a cubic cell of length L, subject to periodic boundary conditions (PBC).[37,48] The one-electron orbitals are linear combinations of a periodic plane-waves basis. An Ewald summation accounts for the electrostatic interactions, where the $Q=0$ term cancels out between the various interaction types for neutral species.[37] The maximum wave number $G_{\max}$ in each Cartesian direction (x,y,z) limits the description of kinetic energy. Alternatively and equivalently (under the same boundary conditions), the orbitals can be represented via their R-space values on grid-points of an equally spaced mesh in the cubic cell. The grid spacing δx in each direction is related to the maximum wave number by: $\delta x = \pi / G_{\max}$.

Even if core electrons are discarded from the electronic structure problem, for example, by using a frozen core approximation or effective core pseudopotentials, the valence orbitals are still difficult to describe with plane waves because of the high kinetic-energy components near the atomic core. This dictates the use of soft pseudopotentials, which smooth the valence orbitals near the ionic core leaving intact their form outside the core. It is important to emphasize the difference between effective core potentials and soft pseudopotentials. The latter have the role of smoothing the valence orbitals, in addition to eliminating core electrons. Thus, even for the hydrogen atom, where there are no core electrons, it is beneficial to use soft pseudopotentials.

TABLE I. HF-SCF atomization energies (eV) vs cell length L of H_2 ($R_{\text{H–H}}=1.4$ Bohr) BeH_2 (linear, $R_{\text{H–Be}}=2.5$ Bohr) and Be_2 ($R_{\text{Be–Be}}=4.70$ Bohr). Results based on GGA-PP, using grid spacing $\delta x = 0.5$ a.u. For comparison, estimates of the atomization energies of these systems based on SCF computations not using pseudopotentials are quoted.

L(a.u.)=	16	24	32	∞[a]	SCF
$D_e(H_2)$	3.88	3.81	3.78	3.74	3.64 (Ref. 56)
$D_e(BeH_2)$	5.66	5.76	5.79	5.80	5.45 (Ref. 57)
$D_e(Be_2)$	−0.347	−0.241	−0.254	−0.265	−0.33 (Ref. 46)

[a] Estimated by extrapolation.

Generalized nonlocal, norm-conserving pseudopotentials,[49] expressed in the Kleinman–Bylander (KB) separable form,[50] describe the interaction potential of a valence electron with the ionic cores. A computer program written by Fuchs and Scheffler[51] generates the pseudopotentials while eliminating the formation of ghost states.[52] The pseudopotential is essential for efficient use of the plane-waves basis because it smoothes the valence orbitals near the ionic cores, thus allowing for a large value of δx. This in turn changes the form of the valence orbitals in the region of the ionic cores. Great care is taken in constructing the pseudopotential to prevent this effect from affecting the form of the valence orbitals outside a cutoff radius around each ion. The pseudopotentials are optimized for a DFT computation, and it is an important question whether this scheme gives accurate atomization energy when a valence correlated electronic structure method is used.

The HF-SCF energy in this representation is required to converge with respect to two parameters: The grid spacing δx and the cell size L. It is found that the convergence with respect to grid spacing δx is rapid once a value smaller than a critical spacing is used. The value of the critical δx depends on the pseudopotential and we used the Troullier–Martins (TM) method[53] to generate pseudopotentials for hydrogen and beryllium. The generated pseudopotentials were of two types, depending on the level of theory used for the atomic computation: LDA[54] (LDA-PP) and GGA[54,55] (GGA-PP).

The HF-SCF atomization energies of H_2, BeH_2, and Be_2 based on the GGA pseudopotentials are shown in Table I.[56,57] Notice the negative values of De for Be_2 indicating that the molecule is unstable in the Hartree–Fock theory (in fact, the Hartree–Fock potential curve is everywhere repulsive[46]).

We also performed computations using the LDA based pseudopotential (LDA-PP). In general, it is found that the Hartree–Fock atomization energies differ in the three cases. Specifically, the following inequality relating Hartree–Fock atomization energies based on LDA and GGA pseudopotentials, and accurate all-electron computations (labeled ''HF/Full''), reported in literature was found:

$$D_{\text{HF/LDA-PP}} > D_{\text{HF/GGA-PP}} > D_{\text{HF/Full}}. \tag{2.1}$$

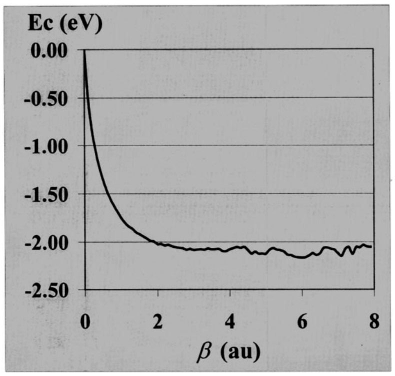

FIG. 1. Recovered correlation energy of BeH_2 in a cubic cell of length $L=6$ a.u. and grid spacing $\delta x=0.5$ a.u. after 6000 iterations as a function of β.

GGA/LDA based pseudo cores are not strictly expected to yield exact HF-SCF energies. Indeed they do not as seen in the table. A proper pseudopotential should give accurate total atomization energy so it is anticipated that the correlation energy will correct the discrepancy. As we shall see this is not fully obtained.

III. SC-AFMC CORRELATION ENERGY

The SC-AFMC enables the computation of the temperature-dependent electronic energy[33]

$$E(\beta)=\frac{\langle\Phi_0|\hat{H}e^{-\beta\hat{H}}|\Phi_0\rangle}{\langle\Phi_0|^{2-\beta\hat{H}}|\Phi_0\rangle}, \tag{3.1}$$

where $\Phi_0=|\phi_1\cdots\phi_N|$ is the Hartree–Fock determinant of the occupied molecular orbitals ϕ_k. $E(\beta)$ asymptotically approaches an exponential decay to the ground state as β is raised

$$E(\beta)\rightarrow W(\beta)=E_{gs}+Ae^{-\Delta E\beta}\Delta E, \tag{3.2}$$

where E_{gs} is the ground-state energy and ΔE is an excitation energy to the closest excited state not orthogonal to the determinant Φ_0. Thus, a least-squares fit of the computed energy $E(\beta)$ to an exponential is made (see Fig. 1, for example). Once the parameters of the fit are determined, the statistical error is computed by

$$SE(N)=\sqrt{\frac{1}{N}\sum_{n=1}^{N}[E(\beta_n)-W(\beta_n)]^2}. \tag{3.3}$$

Determining the appropriate value of β is not straightforward. Typically, one strives for $\beta\Delta E\gg 1$ as this condition validates a correct fit using Eq. (3.2). However, estimates of ΔE (based, for example on the Hartree–Fock computation) are not always reliable, especially when ΔE is small. Crucially though, a small value of ΔE signals the existence of nondynamical correlation, which in turn increases the statistical error at large β. This is because when nondynamical correlation exists, the Hartree–Fock density is no longer a good approximation to the true density, making it an inappropriate stabilizing contour-shift.[33] A rather unfortunate situation transpires: A large β computation is unachievable exactly when it is needed. The situation can be remedied by using a multireference method to compute the density. Until such an attempt is made, the computational accuracy for systems with nondynamical correlation is restricted. In the computations described below the Be_2 system is such a problematic system. By comparing the results we obtained with other computations, we believe (but cannot prove) that we have collected most of the correlation energy also for this system.

TABLE II. Correlation energy and decay constant ΔE (both in eV) for H_2 vs cell size L. Based on: GGA-PP and $\delta x=0.5$ a.u. N is the number of iterations and β is the final time.

L (a.u.)	E_{corr}	N	β (a.u.)
8	0.99(2)	3000	5
12	1.06(2)	3000	5
16	1.05(2)	3000	5

An additional word on time evolution and the SC-AFMC time step $\Delta\beta$. Throughout the computations, a value of $\Delta\beta=0.1$ a.u. was used. The ensuing discretization error is unnoticeable relative to the reported statistical errors. The operation of the evolution operator $\hat{U}(\beta,\beta+\Delta\beta)$ propagating an orbital ϕ_k from imaginary time $t=\beta$ to $t=\beta+\Delta\beta$ is performed by the Chebyshev expansion method of Kosloff and Tal-Ezer.[58] This algorithm is essentially of machine accuracy when the evolution is holonomic. Thus the only discretization error is due to the noncommutativity of the time-dependent auxiliary-field Hamiltonian with itself at different times within the small interval $\Delta\beta$.

The length of the Chebyshev expansion is proportional to $\Delta\beta\Delta H$ where ΔH is the spectral range of the auxiliary-field Hamiltonian. In traditional AFMC, where there is no contour shift, ΔH is determined by the bare pseudopotential and can be large. Thus time evolution is numerically expensive. Because in SC-AFMC the atomic core is partially screened by the shifting field the spectral range of the auxiliary Hamiltonian is smaller and time evolution is less demanding. The typical number of terms of the expansion in the computations is between 15 and 20 terms.

A. H_2 correlation energy

Unlike the HF-SCF energy, the correlation energy of H_2 converges rapidly with cell size to the value $E_c(H_2)=1.05\pm0.02$ eV, as seen in Table II. The statistical error of 0.02 eV was achieved with 3000 iterations.

The H_2 correlation energy based on a full core computation is[59] 1.11 eV. Thus the bond correlation energy under a pseudopotential underestimates the true correlation energy. This corrects the overestimation of the HF-SCF atomization energy by the pseudopotential discussed previously, making the total electronic atomization energy only 0.02 eV larger than the correct H_2 atomization energy.

B. Be valence correlation energy

An example of the temperature dependent electronic energy of Be after 8000 SC-AFMC iterations is shown in Fig. 1. It is seen that the cure is well fitted by an exponential $W(\beta)$ for time $\beta>1$ a.u. After performing a fit the statistical error is defined in Eq. (3.3). The cell size dependent valence

TABLE III. Be valence correlation energy (eV) vs cell size L. Based on GGA-PP and a grid spacing of $\delta x = 0.5$ a.u. N is the number of iterations and β is the final time. Numbers in parentheses are statistical errors in the last digits.

L (a.u.)	E_{corr}	N	β (a.u.)
8	0.64(2)	8000	10
12	1.16(2)	8000	10
16	1.32(3)	12000	10

correlation energy of the Be atom shown in Table III from which the extrapolated value of $E_c = 1.33 \pm 0.03$ eV is deduced. This should be compared to $E_c = 1.255$ eV—the extrapolated valence correlation energy calculated by Martin[60] using a coupled-cluster singles and doubles method [equivalent to full CI (configuration interaction) in this case].

C. BeH$_2$ valence correlation energy

The valence correlation energy of the BeH$_2$ molecule is shown in Table IV. Both correlation energy and decay constant are less sensitive to the cell size than the Be atom.

The valence correlation energy is $E_c(\mathrm{BeH_2}) = 2.14(3)$ eV. This value is obtained by extrapolation and should be compared to 2.19 eV, the valence correlation energy reported by Martin[60] using cc-pVnZ type basis sets used in a coupled cluster approximation which includes all single-, double-, and an approximate treatment of triple excitations [CCSD(T)].[61]

Our calculated bond valence correlation energy is 0.80(3) eV, a value comparable to 0.93 eV deduced by Martin[59] using CCSD(T). Martin shows that the contribution of core electrons to the correlation energy is only ~5% of this value, comparable to the statistical sampling error.

D. Valence correlation energy of Be$_2$

In order to stabilize the SC-AFMC integration, a good approximation is needed to the fully correlated one-electron density matrix.[33] In many cases, the Hartree–Fock density is used satisfactorily. However, for Be$_2$ substantial nondynamical correlation exists, due to the small energetical difference between $2s$ and $2p$ levels[45] (see Ref. 62 for an interesting discussion concerning the definition of nondynamical correlation). Here, the Hartree–Fock density is not a good approximation to the correlated density because the Hartree–Fock determinant is not dominant in the ground-state wave function. The correlation energy of Be$_2$ is, therefore, difficult to compute via conventional SC-AFMC because the stabilization is made with a Hartree–Fock determinant. The value $\beta = 12$ a.u. used is dictated by the size of the Monte Carlo fluctuations. It is expected (although we have not checked this) that a better approximation to the density can significantly reduce the statistical fluctuations and a larger value of β will be reached.

TABLE IV. BeH$_2$ valence correlation energy (eV) vs cell size L. Based on GGA-PP and $\delta x = 0.67$ a.u. N is the number of iterations and β is the final time. Numbers in parentheses are statistical errors in the last digits.

L (a.u.)	E_{corr}	N	β (a.u.)
8	2.12(2)	5000	6
12	2.13(3)	5000	6

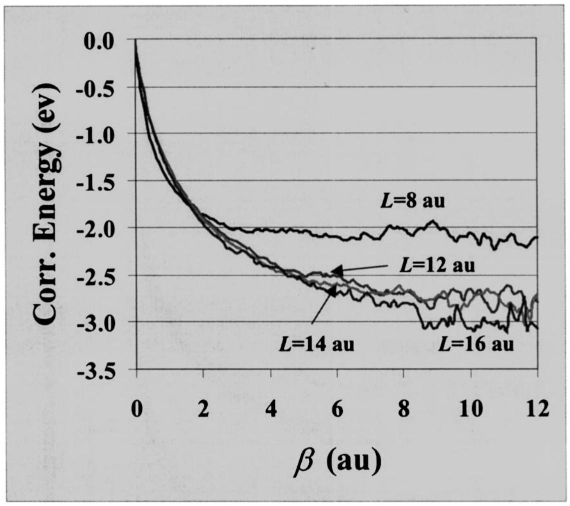

FIG. 2. Monte Carlo correlation energy as a function of inverse temperature for Be$_2$ in various cell lengths $L = 8,12,14,16$ a.u. (from top to bottom).

The Monte Carlo energy, fluctuations and dependence on inverse temperature and the cell size are shown in Fig. 2. It is seen that for the smallest cell shown, the statistical fluctuations are small indicating that the multireference nature of the problem is sensitive to cell size. This is reasonable as cell size affects energy level spacing of a particle in cell.

The valence-correlation energy of Be$_2$ is shown for various cell lengths in Table V. Due to the large statistical error, it is difficult to determine precisely the correlation energy. At a cell length of 16 a.u. the valence correlation energy is $-2.95(15)$ eV. This leads to bond valence-correlation energy of 0.3 (2) eV, which in light of the large statistical error compares reasonably well with the extrapolated value of 0.43 eV estimated by Martin[46] using a highly accurate coupled cluster approximation.[63]

IV. SUMMARY

A new quantum Monte Carlo method has been presented for electronic structure computations using norm-conserving pseudopotentials and plane-waves. The method is shown capable in principle of high accuracy description of chemical bonds as shown in Table VI.

The adequacy of norm-conserving pseudopotentials to describe the interaction with atomic cores in a fully corre-

TABLE V. Be$_2$ valence correlation energy (eV) vs cell size L. Based on GGA-PP and $\delta x = 0.5$ a.u. N is the number of iterations. Numbers in parentheses are statistical errors in the last digits.

L (a.u.)	E_{corr}	N
8	2.21(3)	6000
12	2.68(10)	9000
14	2.75(10)	7000
16	2.95(15)	8000

TABLE VI. Atomization energy (eV) of systems discussed in the text. Numbers in parentheses are statistical errors in the last digits.

	SCF GGA-PP	Total GGA-PP	CC/CI
H_2	3.69	4.74(2)	4.75[a] (Ref. 59)
BeH_2	5.80	6.60(4)	6.42[a] (Ref. 57)
Be_2	−0.27	0.0(2)	0.11[a] (Ref. 46)

[a] Includes estimates of core-valence and core–core correlation contributions.

lated electronic structure computation was another issue we set to examine here. Our results show that the quality of atomization energies depend on the level of theory used to develop the pseudopotential. A pseudopotential based on GGA consistently gives better results than pseudopotential based on LDA. When comparing HF-SCF atomization energies based on LDA/GGA pseudopotentials ($D_{\mathrm{HF/LDAPP}}$ and $D_{\mathrm{HF/GGAPP}}$) with all-electron full core energies $D_{\mathrm{HF/Full}}$, we find a systematic trend

$$D_{\mathrm{HF/LDAPP}} > D_{\mathrm{HF/GGAPP}} > D_{\mathrm{HF/Full}}. \tag{4.1}$$

We believe that the DFT based pseudopotentials limit the accuracy of the explicitly correlated atomization energy to around 0.2 eV (for the systems studied here). Thus, one important future direction of this project is the inclusion of core and core-valence correlation effects, when they are expected to be important. This can be done using the CPP of Shirley and Martin[22] (the V_{e-e} part of the CPP can also be treated because the AFMC method can in principle treat any type of two-body interaction).

We found that correlation energy generally converges faster than the Hartree–Fock energy as cell length is increased. We conclude that smaller cells are needed for the extensive correlated computation. In H_2 and BeH_2 correlation energy converged at smaller cell lengths than the correlation energy of Be and Be_2. The latter systems exhibited nondynamical correlation (also seen as increased statistical errors). This shows that when nondynamical correlation exists the correlation effects are less localized.

An additional problem we encountered is the slow convergence of correlation energy in Be_2 with respect to the propagation time. We suspect that this problem too is directly associated with the presence of nondynamical correlation. Thus, an important future direction is the development of specialized methods to allow SC-AFMC to deal with this problem.

The computational labor invested in the SC-AFMC stage is extensive. Typically, the QMC computation on these small molecules consumes one to two orders of magnitude more CPU time than a CCSD(T) based computation. We anticipate the tables to be turned once larger systems are treated. This, however, remains to be explored in future applications of the method.

ACKNOWLEDGMENTS

R.B. expresses appreciation to E. R. Davidson, J. M. L. Martin, M. Head-Gordon, N. Govind, S. Alvarez, E. Ruiz, and R. Kosloff for their invaluable comments and suggestions. R.B. gratefully acknowledges the assistance, support, and encouragement offered by A. Ben-Shaul and M. Asscher at the Hebrew University. We also express thanks A. Barak and R. Chermoni for their help with the MOSIX cluster.

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