

Systematically convergent method for accurate total energy calculations with localized atomic orbitals

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We introduce a method for solving a self-consistent electronic calculation within localized atomic orbitals that allows us to converge to the complete basis set (CBS) limit in a stable, controlled, and systematic way. We compare our results with the ones obtained with a standard quantum chemistry package for the simple benzene molecule. We find perfect agreement for small basis set and show that, within our scheme, it is possible to work with a very large basis in an efficient and stable way. Therefore we can avoid to introduce any extrapolation to reach the CBS limit. In our study we have also carried out variational Monte Carlo and lattice regularized diffusion Monte Carlo with a standard many-body wave function defined by the product of a Slater determinant and a Jastrow factor. Once the Jastrow factor is optimized by keeping fixed the Slater determinant provided by our scheme, we obtain a very good description of the atomization energy of the benzene molecule only when the basis of atomic orbitals is large enough and close to the CBS limit, yielding the lowest variational energies.

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I. INTRODUCTION

The use of localized basis sets is becoming more and more important in several electronic-structure methods because it allows a dramatic reduction in the dimension N of the single-particle basis, i.e., much smaller than standard plane-wave basis set dimensions. For instance in quantum chemistry calculations it is very difficult, if not impossible, to use post-Hartree-Fock methods with extremely large basis sets because their computational cost scales with a large power of N (N^4 – N^7). On the other hand all linear scaling methods^{1–4} are based on a suitably localized basis and exploit the fact that the matrix elements of the Hamiltonian decay very rapidly with the distance among the orbital centers. Several other applications are known, and it is basically impossible to list all of them.

Although our findings apply generally to all the above issues, in this paper we focus, in particular, on the use of a localized basis set for Monte Carlo optimization of wave functions (WFs) because the number of variational parameters—e.g., in a Slater (S) determinant—is proportional to N , and only with a localized basis it remains in a reasonable range even for large systems. Therefore, thanks to the recent advances in the optimization techniques in quantum Monte Carlo (QMC) calculations,^{5–8} it is possible nowadays to optimize a full many-body wave function with an affordable computational time (proportional to N^3 – N^4).

Despite the use of localized basis sets is becoming more and more popular there is an important issue on how to converge to the so-called “complete basis set” (CBS) limit. In plane-wave calculations this is usually achieved by systematically increasing the kinetic-energy cutoff so that a reliable and very well-controlled convergence is possible. Unfortunately within a localized basis set framework, until now it is not possible to reach the same level of accuracy of the plane-wave approach because a too large value of N leads to redundancy of the basis and typically to numerical instabilities.

On the other hand, working with a small basis far from the CBS limit, leads to the well-known basis superposition error, that deteriorates the accuracy in the description of the chemical bond.

The difficulty to work with a localized basis of N nonorthogonal orbitals $\phi_i(\vec{r})$ ($i=1, \dots, N$) can be quantified by considering the $N \times N$ overlap matrix,

$$S_{i,j} = \langle \phi_i | \phi_j \rangle = \int d^3\vec{r} \phi_i(\vec{r}) \phi_j(\vec{r}). \quad (1)$$

In the following we assume that the atomic orbitals are normalized so that the diagonal elements of the above overlap matrix are identically equal to one. Since this is an overlap matrix it is also positive definite, namely, all its eigenvalues s_i , henceforth assumed in ascending order, are positive $s_i \geq 0$, and a vanishing eigenvalue occurs only if the orbitals are linearly dependent.

If the condition number of this positive definite matrix, namely the ratio $s_{cond} = \frac{s_N}{s_1}$ between the largest s_N ($s_N < N$, as the trace of S is $\sum_i S_{i,i} = \sum_i s_i = N$) and the lowest eigenvalue s_1 is below a certain threshold, calculations are very difficult and the convergence to the CBS limit is impossible to reach with standard methods. This problem has been often circumvented by extrapolation procedures and/or relying on cancellation errors.^{9–12} However we believe that, at least for a simple self-consistent field (SCF) calculation based on the density-functional theory (DFT) within the standard local-density approximation (LDA), it is very important to converge to the CBS limit, essentially in the same way as in a plane-wave calculation.

Here we show that this important task can be achieved by applying a simple strategy for the diagonalization of the Hamiltonian, strategy that can be applied to any SCF calculation. Moreover we find that, even for the atomization energy of the simple benzene molecule, it is necessary to work close to the CBS limit in order to obtain a well converged

result because, at least in this case, energy differences approach the CBS limit only slightly faster than the total energy.

In this work, as already mentioned, we are interested to combine the Slater determinant obtained by an SCF calculation with a so-called Jastrow factor, also expanded in a localized basis $\phi_i(\vec{r})$. In this way an accurate many-body wave function is defined, that typically describes rather well the electron correlation, often much better than the original SCF calculation. Indeed in our QMC calculations, we have also found that it is very important to use a very large basis set for the DFT Kohn-Sham (KS) orbitals because only in this case the corresponding Slater determinant is very close to the optimal one, namely, the one that minimizes the energy in presence of the Jastrow factor. After that we obtain a very accurate atomization energy for this simple molecule, that is compatible with the experiments, despite our strong restriction of the variational ansatz.

The paper is organized as follows. In Sec. II we describe the basis of localized atomic orbitals and the variational wave function used in this work, we briefly review the SCF LDA method and we show how to work with a large basis of localized atomic orbitals. In Sec. III we present our results for the benzene molecule and finally in Sec. IV we draw our conclusions.

II. COMPUTATIONAL DETAILS

A. Localized basis set

In our DFT LDA-based calculations, we have used S exchange and Perdew¹³ correlation functionals. The KS equations are solved by expanding the electronic orbitals in a Gaussian-type orbital (GTO) basis set. Only four valence electrons are taken into account for the carbon atom. The 1s core electrons are considered by atomic pseudopotentials that are also used for the hydrogen atom in order to eliminate the divergent electron-ion attraction at short distance.¹⁴

In the test calculation presented here, we consider the benzene molecule with experimental carbon and hydrogen atomic positions. We define a localized basis set centered on each atom by using simple Gaussians $\exp(-Z_i r^2)$ with given angular momentum: s, p, d, f, g, \dots . In order to achieve convergence in a systematic way we define the standard even-tempered sequence for GTO exponents Z_i ,

$$Z_i = \alpha\beta^i \quad (2)$$

for $i=0, \dots, n_l-1$ with $\alpha=Z_{\min}$ and $\alpha\beta^{n_l}=Z_{\max}$, where n_l is the number of exponents used for the angular momentum l . The maximum number n of exponents is used only on the s -wave channel $n_0=n$, whereas for the higher angular momenta $l=1, 2, 3, 4, \dots$ the number of exponents n_l is smaller and is given by following choice:

$$n_l = n_0 - 2l. \quad (3)$$

Notice that the value of β is implicitly defined by the choice of Z_{\max} that will be discussed in the following.

This basis is obviously complete as long as n and the maximum l ($l \leq l_{\max}$) are systematically increased until con-

vergence is reached. The obvious advantage of our even-tempered GTO set is that the exponent sequence is determined by only two parameters, Z_{\max} and Z_{\min} . Our purpose is indeed to show that a systematic convergence with n and $l_{\max} \leq 4$ can be obtained by using a large but not prohibitive value of n . In practice for large n , the SCF energy is almost independent on Z_{\max} and Z_{\min} and therefore the choice of these two parameters can be done by optimizing the DFT energy for few test cases and by checking the stability of these two parameter values for large n . As a result we have verified that the simple choice $Z_{\min}=0.2$ and $Z_{\max}=10$ is nearly optimal for all n in the benzene case, as well as for the carbon atom. We have therefore adopted these two parameter values in all the forthcoming calculations. Probably by optimizing all exponents much faster convergence can be obtained but in this work we want to emphasize that it is possible to work with a large basis set, deliberately larger than necessary because not fully optimized, and obtain accurate and systematically converging results without limitations or constraints, likewise a plane-wave-based approach. As a result we show that we can achieve this task by using n as large as ≈ 30 , that represents a very important restriction of the dimension N of the basis, roughly two or three orders of magnitude smaller compared to a plane-wave-based approach with the same accuracy in the total energy, e.g., an accuracy of 0.1 mH in the total energy of the benzene molecule can be achieved with $N \approx 1000$ localized orbitals, whereas at least 200^3 plane waves are necessary for the same target.

B. Description of the SCF method

The DFT functional, within the LDA approximation, can be evaluated on a given set of atomic orbitals $\phi_i(\vec{r})$ and is then defined by the overlap matrix S in Eq. (1) and the one body Hamiltonian matrix elements,

$$H_{i,j} = \langle \phi_i | H^{1b} | \phi_j \rangle + \langle \phi_i | v_H + v_{xc} | \phi_j \rangle, \quad (4)$$

where H^{1b} contains kinetic energy, electron-ion interaction, and the pseudopotentials used, whereas v_H and v_{xc} are the Hartree and the exchange and correlation potentials, respectively, both defined only by the total electronic density $n(\vec{r})$. In this nonorthonormal basis the Kohn-Sham orbitals are given by

$$\psi_i(\vec{r}) = \sum_j \chi_{ij} \phi_j(\vec{r}), \quad (5)$$

where the coefficients $\chi_{i,j}$ can be obtained by solving the generalized eigenvalue problem,

$$\sum_j H_{i,j} \chi_{j,i} = E_i \sum_j S_{i,j} \chi_{j,i}. \quad (6)$$

The density is in turn defined by occupying the Kohn-Sham orbitals up to the Fermi energy E_F

$$n(\vec{r}) = \sum_{E_i \leq E_F} 2 \psi_i^*(\vec{r}) \psi_i(\vec{r}) \quad (7)$$

and self-consistency is reached when the output density obtained after the diagonalization coincides within numerical

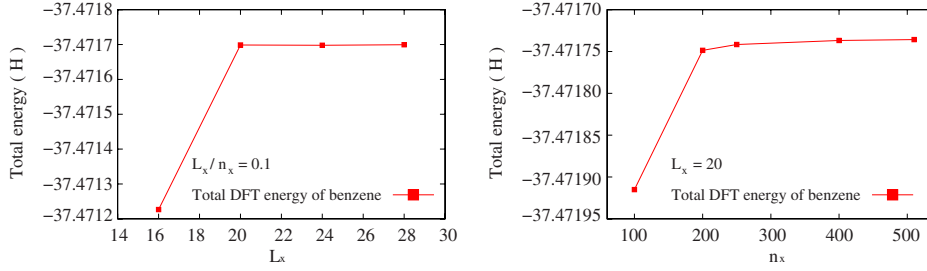


FIG. 1. (Color online) Convergence of the total DFT energy of the benzene molecule as function of the box size L_x (left), in (bohr), and the mesh size n_x (right) using the $8s6p$ even-tempered basis set described in the text.

accuracy with the input density used to evaluate v_H and v_{xc} .

In recent years computer performances have substantially increased and the calculation of overlap and Hamiltonian matrices elements of the above types can be done rather efficiently by straightforward integration over a mesh, e.g., by replacing the integrals with appropriate summations over a set of electronic positions \vec{r}_l uniformly distributed in a finite volume $V=L_x \times L_y \times L_z$, spanned by $n_x \times n_y \times n_z$ mesh points referred to the x, y, z Cartesian axes, respectively, namely,

$$S_{i,j} = v \sum_l \phi_i(\vec{r}_l) \phi_j(\vec{r}_l),$$

$$H_{i,j} = \frac{1}{2} v \sum_l \{ \phi_i(\vec{r}_l) [H^{\text{KS}} \phi_j(\vec{r}_l)] + [H^{\text{KS}} \phi_i(\vec{r}_l)] \phi_j(\vec{r}_l) \}, \quad (8)$$

where $H^{\text{KS}} = H^{\text{b}} + v_H + v_{xc}$ is the Kohn-Sham Hamiltonian and $v = \frac{L_x L_y L_z}{n_x n_y n_z}$ is the elementary box volume of the mesh grid. Notice that in the above discretization of the integrals we have symmetrized the Hamiltonian matrix elements, thus restoring the Hermitian property of the Hamiltonian ($H_{i,j} = H_{j,i}$) even for a finite mesh.

Further important improvements have been introduced to allow a fast and efficient convergence of these matrix elements by increasing the box volume and the size of the mesh ($n_x, n_y, n_z \rightarrow \infty$). For instance the origin of the mesh grid was chosen in a way to maximize the minimum distance between the mesh and the ion positions. Moreover the Hartree potential in atomic units was calculated by the convolution,

$$v_H(\vec{r}_j) = v \sum_{l \neq j} 1/|\vec{r}_l - \vec{r}_j| n(\vec{r}_l) + C n(\vec{r}_j) = 1/V^A \sum_q v_q^c n_{-q}, \quad (9)$$

where n_q and v_q^c are the density and the Coulomb potential Fourier transform, respectively, whereas the finite constant C takes into account the infinite contribution of the Coulomb potential for $\vec{r}_l = \vec{r}_j$, in a way that will be discussed later on. For open systems, the convolution was computed on a box of twice linear dimension with volume $V^A = 8V$ and with the origin $\vec{r} = (0, 0, 0)$ at the center of the box, namely, $n_x \rightarrow 2n_x$, $n_y \rightarrow 2n_y$, $n_z \rightarrow 2n_z$ and $|x| \leq L_x$, $|y| \leq L_y$, $|z| \leq L_z$. The convoluted density $n(\vec{r})$ is assumed to vanish in V^A outside the physical volume V ($0 \leq x \leq L_x, 0 \leq y \leq L_y, 0 \leq z \leq L_z$) because the charge density is decaying exponentially fast at large distance from the atoms. Then it is defined periodic with period $(2L_x, 2L_y, 2L_z)$ so that wave vectors q are correspondingly quantized $q = (\pi/L_x n, \pi/L_y m, \pi/L_z l)$ with integers n, m, l , and the standard and extremely efficient con-

volution algorithm based on fast Fourier transform can be applied, with $v_q^c = \sum_{r_j \in V^A, r_j \neq 0} v / |\vec{r}_j| e^{-iqr_j} + C$. By using this enlarged box V^A , we can avoid to add fictitious contributions to the Hartree potential that would have raised from nonvanishing replicas with shorter periodicity (L_x, L_y, L_z) . It is also simple to show that in the limit $n_x, n_y, n_z \rightarrow \infty$, the Hartree potential coincides with the exact integral expression in the physical volume V , where we solve the eigenvalue equations in Eq. (6). Finally, in order to have an efficient extrapolation for $n_x, n_y, n_z \rightarrow \infty$ at fixed volume, we have adopted a regularization for the Coulomb potential when $r_l = r_j$ for open systems. This is obtained by using an appropriate constant C that is determined by imposing that the Hartree potential at $r=0$ coincides with the exact one for a Gaussian density $n(\vec{r}) = \exp(-r^2/2)$, namely, $v_H(0) = \int dr^3 1/r \exp(-r^2/2) = C + v \sum_{r_l \in V^A, r_l \neq 0} \exp(-r_l^2/2)/r_l = 4\pi$ in this case.¹⁵ Obviously $C \rightarrow 0$ for $n_x, n_y, n_z \rightarrow \infty$ and therefore this regularization is only meant to accelerate the convergence but does not change the limit values of all the quantities computed with this SCF method.

All the above simple technical improvements allow us to have a very rapidly convergent calculation in $n_x, L_x \rightarrow \infty$ that is otherwise almost impossible, especially for open systems. In our application to the benzene molecule we have chosen a cubic box ($n_x = n_y = n_z$ and $L_x = L_y = L_z$) and the convergence vs the box $L_x \rightarrow \infty$ and mesh $n_x \rightarrow \infty$ size are displayed in Fig. 1.

In Table I, we show the same type of convergence also for the exchange and correlation energies. It is clear that the rapid convergence of our method applies also to correlation functions and also that high-quality results can be obtained with a reasonable computational effort.

The way we compute matrix elements on a grid is obviously much less efficient than the standard way to use tabulated Gaussian integrals.¹⁶ Nevertheless the calculation we propose is quite simple and straightforward, obviously at some expense of computer time, but with the remarkable

TABLE I. Total, exchange, and correlation energies of DFT calculation of the benzene molecule using $24s22p10d6f$ basis set. A cubic box ($L_x = L_y = L_z$) is used. The given values of energies and box sizes are in (H) and (bohr), respectively.

n_x	L_x	Total energy	Exchange energy	Correlation energy
160	16	-37.5404624	-10.6865190	-1.5922693
200	20	-37.5400762	-10.6867874	-1.5922738
240	24	-37.5400821	-10.6867701	-1.5922721
400	20	-37.5400657	-10.6867885	-1.5922732

advantage that this method can be applied also to non-Gaussian orbitals, to periodic system, and that the accuracy of the calculation can be systematically controlled by increasing n_x and the volume V . This is particularly important when the condition number s_{cond} becomes extremely large, and, for an accurate calculation, both overlap and Hamiltonian matrix elements have to be calculated with much higher accuracy. Moreover, for application to QMC computation, the time spent for a SCF calculation represents only a negligible amount so that it is not really important that this part of the calculation is fully optimized. The most important problem we have solved in this work is the stabilization of the diagonalization routine for arbitrary large basis set and given (namely, allowed by double precision arithmetic) accuracy in the calculation. This technique will be described in details in the next section.

C. Stable diagonalization routine

In this part we describe our way to improve the accuracy of the SCF algorithm by means of a more stable numerical solution of the generalized eigenvalue equations given in Eq. (6). Basically the task is to compute in a stable way the eigenvectors of the Hamiltonian defined in a nonorthogonal basis of large linear dimension N . The problem is that the overlap matrix S in Eq. (1) may have a very large condition number and a straightforward diagonalization leads to inaccurate and often dirty eigenvectors. In parallel computation there is also the further complication that it is difficult to preserve orthogonality (and accuracy) of eigenvectors without having a huge buffer memory at disposal, as no efficient memory distribution is possible for the orthogonalization procedure. Here we describe the algorithm of our diagonalization routine that solves in a very simple and efficient way all the above computational issues.

(1) We apply first a diagonalization algorithm to the overlap matrix, based on the Householder tridiagonalization and iterative Givens transform to the resulting tridiagonal matrix. All these transformations are unitary and should preserve orthogonality of eigenvectors v_j^i for $i, j = 1, \dots, N$ in infinite precision arithmetic. However this is not the case in practice since the matrix can be very ill conditioned. Therefore, in order to improve the stability of the calculation we follow standard procedures in numerical linear algebra.¹⁷ We disregard eigenvectors with small eigenvalues s_i compared to the maximum one $s_N \leq N$, namely, satisfying $s_i/s_N < \epsilon_{mach}$, where ϵ_{mach} is an input parameter, whose minimum value is around the relative machine precision ($\approx 10^{-16}$ in double precision arithmetic).¹⁸ Neglecting small eigenvectors corresponding to small eigenvalues of the overlap matrix is justified from the fact that an eigenvector of the overlap matrix with nearly zero eigenvalue corresponds to a linear combination of normalized orbitals $\sum_j v_j^i \phi_j(\vec{r})$, satisfying $\sum_j |v_j^i|^2 = 1$, that has almost vanishing norm equal to $\sqrt{s_i}$, i.e., the nonorthogonal basis of normalized orbitals is redundant and this direction can be safely eliminated within an error $\sqrt{s_i}$. Thus after neglecting all these singular directions we obtain a simple bound for the numerical error ϵ_{acc} expected when neglecting all these redundant directions,

$$\epsilon_{acc} < \min_i(\sqrt{s_i} s_i / s_N \geq \epsilon_{mach}) \leq \sqrt{\epsilon_{mach} s_N} \leq \sqrt{\epsilon_{mach} N}, \quad (10)$$

where in the last inequality we have used that $s_N \leq N$, as shown before.

In this step we do not require that the diagonalization has produced really orthogonal eigenvectors but only that the eigenvalues have the right order of magnitude, the normalization of eigenvectors is correct, and that the diagonalization routine has produced linearly independent eigenvectors, properties that are easily satisfied even for extremely singular overlap matrices. Then we define nonsingular directions,

$$e_j^i = \frac{1}{\sqrt{s_i}} v_j^i \quad \text{for } s_i/s_N \geq \epsilon_{mach}. \quad (11)$$

In this basis, the overlap matrix $\tilde{s}_{i,j} = \langle e_i | S | e_j \rangle$ should be equal to the identity in infinite precision arithmetic, namely, a matrix with minimum condition number $s_{cond} = 1$. Thus it turns out that, in finite precision arithmetic, by recomputing $\tilde{s}_{i,j} = \sum_{k,l} e_k^i S_{k,l} e_l^j$ we obtain a well-conditioned matrix that can be diagonalized again with high accuracy,

$$\tilde{s}_{i,j} = \sum_k \tilde{s}_k \tilde{v}_i^k \tilde{v}_j^k \quad (12)$$

and therefore now, analogously to the previous case, we can define directions

$$\tilde{e}_k^i = \frac{1}{\sqrt{\tilde{s}_i}} \tilde{v}_i^k$$

that remain safely orthonormal even in finite precision arithmetic. Finally we store the global transformation from the original basis to the new one

$$U_{i,j} = \sum_k e_j^k \tilde{e}_k^i. \quad (13)$$

In this basis the generalized eigenvalue [Eq. (6)] turns in a standard diagonalization of a very well-conditioned Hamiltonian matrix $\tilde{H} = U H U^\dagger$ because its spectrum corresponds to the physical spectrum of the original Hamiltonian.

(2) At each iteration we recompute the Hamiltonian matrix \tilde{H} in this new basis. (3) Then apply again our diagonalization routine. (4) Go back to the original basis $W_j^i = \sum_k U_{j,k} \tilde{W}_k^i$ for the eigenvectors W_j^i (\tilde{W}_k^i) of H (\tilde{H}), computed at each iteration to implement self-consistency and write the final molecular orbitals in the localized atomic basis set.

The above scheme allows us to obtain a total energy accuracy that, at least in the examples studied in this work, is below 0.1 mH, namely, one order of magnitude smaller than the typical target chemical accuracy. This is achieved in an automatic way, by using $\epsilon_{mach} \approx 10^{-16}$. Namely, even when the basis used is extremely redundant for $N \rightarrow \infty$, the simple algorithm, that we have previously described, allows us to obtain accurate total energies. This solution is general in the following sense: with the present algorithm it is in principle possible to work with arbitrarily large value of the basis dimension N , namely, even with an overcomplete basis set and, after removing redundant directions as described in the first

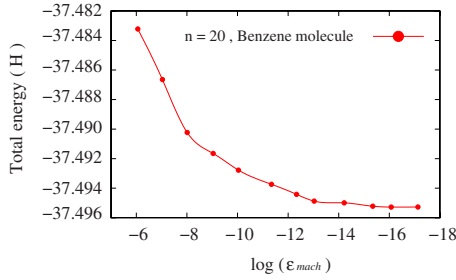


FIG. 2. (Color online) Total DFT energy of benzene molecule in $n=20$ case as a function of our regularization cutoff ϵ_{mach} .

step of the algorithm, we can work with a well-conditioned orthonormal basis, obtained after the second diagonalization, and that provides for large N converged results within the numerical accuracy ϵ_{acc} possible with the available numerical precision. Since, as shown before in Eq. (10), ϵ_{acc} increases very slowly with N , namely, at most as $\propto \sqrt{N}$, we do not expect accuracy problems with basis sets much larger than the ones used in the examples presented here, even within double precision arithmetic.

As shown in Fig. 2, the accuracy can be also controlled by decreasing the value of ϵ_{mach} , a lower value leads to a more accurate calculation, until one reaches a threshold below the relative machine precision when instabilities occurs in the diagonalization because the numerical accuracy of finite precision arithmetic is simply not enough. Better accuracies could be in principle possible only with more accurate operations, e.g., by using quadruple precision. Nevertheless, as anticipated, this algorithm provides a reasonable accuracy in the total energy with standard, and usually much more efficient, double precision arithmetic.

D. Correlated variational wave function for QMC calculations

In this part we describe our WF which has been used in QMC calculations. The usual trial WF used in QMC calculation is the product of an antisymmetric part and a Jastrow factor. The antisymmetric part is a single Slater determinant while the Jastrow factor is a bosonic many-body function which accounts for the dynamic correlations in the system. Our Slater determinant is obtained with $N_{el}/2$ (N_{el} is the total number of electrons in the system) doubly occupied molecular orbitals $\psi_j(r)$, expanded in atomic orbitals as described in Eq. (5). The molecular orbitals are obtained from the self-consistent DFT-LDA calculations explained in the previous section. The Jastrow factor takes into account the electronic correlation between two electrons and is conventionally split into an homogeneous interaction J_2 depending on the relative distance between two electrons, and a nonhomogeneous contribution depending on the positions of one or two atoms, J_3 and J_4 , respectively. It also contains a one particle term J_1 that is important to compensate the change in the one particle density induced by J_2 , J_3 , and J_4 , as well as to satisfy the electron-ion cusp conditions. The one- and two-body terms J_1 and J_2 are defined by the following equations:

$$J_1 = \exp \left[\sum_{ia} -(2Z_a)^{3/4} u(Z_a^{1/4} r_{ia}) + \sum_{ial} g_l^a \chi_{al}^J(\vec{r}_i) \right] \quad (14)$$

and

$$J_2 = \exp \left[\sum_{i<j} u(r_{ij}) \right], \quad (15)$$

where i, j are indices running over the electrons and l runs over different single-particle orbitals χ_{al}^J centered on the atomic center a . r_{ia} and r_{ij} denote electron-ion and electron-electron distances, respectively. The corresponding cusp conditions are fixed by the function $u(r) = F[1 - \exp(-r/F)]/2$ (see, e.g., Ref. 19). g_l^a and F are optimizable variational parameters. The three- and four-body Jastrow $J_3 J_4$ are given by

$$J_3 J_4(\vec{R}) = \exp \left[\sum_{i<j} f(\vec{r}_i, \vec{r}_j) \right] \quad (16)$$

with $f(\vec{r}_i, \vec{r}_j)$, being a two-electron coordinate function that can be expanded into the same single-particle basis used for J_1 ,

$$f(\vec{r}_i, \vec{r}_j) = \sum_{ablm} g_{lm}^{ab} \chi_{al}^J(\vec{r}_i) \chi_{bm}^J(\vec{r}_j) \quad (17)$$

with g_{lm}^{ab} optimizable parameters. Three-body (electron ion electron) correlations are described by the diagonal matrix elements g^{aa} , whereas four-body correlations (electron ion electron ion) are described by matrix elements with $a \neq b$.

The exhaustive and complete expression of the Jastrow factor $J(\vec{R}) = J_1(\vec{R}) J_2(\vec{R}) J_3(\vec{R}) J_4(\vec{R})$ that we adopt in this work allows us to take into account not only weak electron-electron interactions but it is also extremely effective for suppressing higher energy configurations occurring when electrons are too close.

III. RESULTS AND DISCUSSION

In this section we show the remarkable convergence and stability properties of our method for the calculation of the total and atomization energies of the benzene molecule in the CBS limit. To this purpose we consider an atomic basis with $l_{max} \leq 1$, namely, with only s and p type of orbitals allowed and show that it is possible to converge to the $n \rightarrow \infty$ case even when, for large n , too many orbitals of the same angular momentum become highly redundant and are difficult to treat with standard methods.

In Fig. 3 we compared our total DFT energies of the carbon atom and the benzene molecule with the ones obtained with the GAUSSIAN09 package.¹⁶ We have used both for GAUSSIAN09 and our DFT algorithm exactly the same basis sets and pseudopotentials, treated with maximum accuracy in the angular integration, and therefore with negligible error, as well as the same Slater exchange and correlation functional with the standard Perdew-Zunger parametrization.¹³

For the small basis sets ($n_s=6,8$) we are in excellent agreement with GAUSSIAN09. However, with large basis sets ($n_s > 8$) there is a clear difference between our results and the GAUSSIAN09 ones. We do not know exactly what is the reason of this discrepancy. We just report that, as it is shown in the lower panels of Fig. 3, the condition number s_{cond} is increasing quite rapidly with the dimension N of the basis set, and the discrepancy between our results and GAUSSIAN09 is evident when the condition number becomes larger than $\approx 10^8$. Moreover since DFT is a variational method, it should be

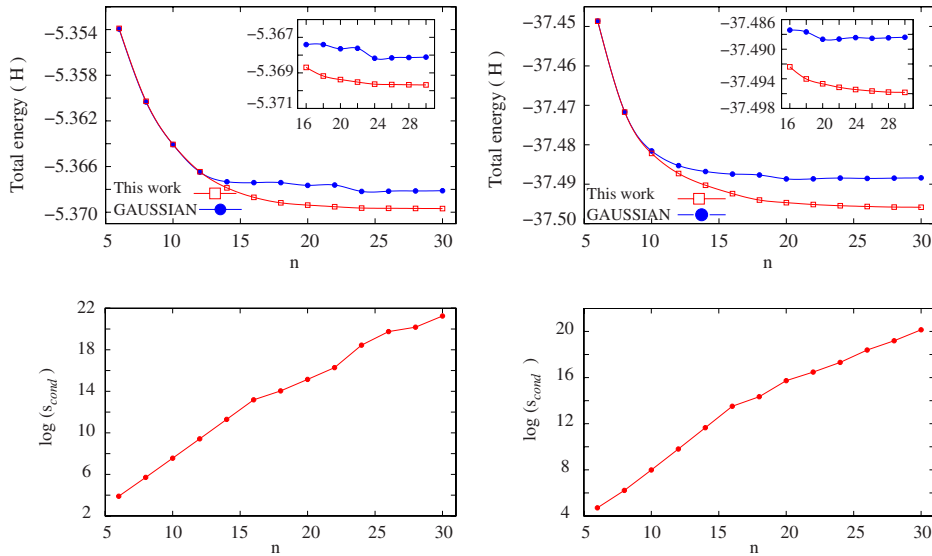


FIG. 3. (Color online) Upper panels: convergence of the total DFT energy of the carbon atom (left) and the benzene molecule (right) using an atomic basis set containing only s and p angular momenta. Results obtained by GAUSSIAN09 are also shown for comparison. Lower panel, logarithm of the condition number s_{cond} of the overlap matrix for the carbon atom (left) and the benzene molecule (right).

clear that for a given basis set the method that provides the lowest value of the functional should be the most accurate, provided the value of the functional can be calculated accurately. Indeed we have verified that a large condition number $s_{cond} \sim 10^{17}$ affects only the self-consistent step [in our case the diagonalization in Eq. (6)] but allows to compute the value of the functional without particular problems.²⁰ Therefore we can safely state that our Kohn-Sham molecular orbitals are very well converged, whereas standard methods suffers to work already with condition number larger than 10^8 .

As a matter of fact our DFT energy for the benzene molecule converges to a very good value $-37.4951453(H)$ [e.g., the GAUSSIAN09 result in the same basis is $-37.4886324(H)$]. The quality of our very well converged molecular orbitals is also evident when we compute the expectation value of the energy of the corresponding Slater determinant by using the standard variational Monte Carlo (VMC) technique to compute the energy expectation values (see Fig. 4). Though it is clearly inefficient to use VMC to compute energy expectation values of uncorrelated wave function, it is useful to use this method in this case because it does not require the explicit evaluation of the matrix S with very large condition number.

Moreover the study of the $n=20$ case as a function of our regularization cutoff ϵ_{mach} , displayed in Fig. 2, clearly shows

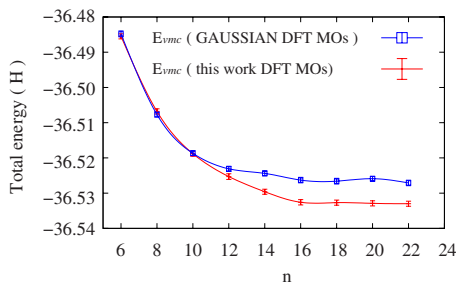


FIG. 4. (Color online) VMC computation of the total energy E_{vmc} of the Slater determinant obtained with Kohn-Sham molecular orbitals. For comparison we show also the results obtained with GAUSSIAN09.

that we can reach a sufficient accuracy (~ 0.1 mH) in the total energy even in the large basis set limit, and that therefore the results for $n=24$ should be considered well converged, namely, close to the $n \rightarrow \infty$, $l_{max}=1$ case.

It is also particularly interesting to show how the atomization energy converges in this case. In Fig. 5 our results clearly indicate that the so-called basis superposition error is very important in this case and monotonically disappears only for large n .

Finally we study the convergence of the total energy as a function of the maximum angular momentum l_{max} of the atomic basis. DFT energies are shown in Table II. Though the difference between $l_{max}=4$ ($spdfg$) and $l_{max}=3$ ($spdf$) is larger than 1 mH, this table shows that the convergence with l_{max} is quite rapid, as each time l_{max} is increased by a unit the accuracy improves by more than a factor 3, and therefore for $l_{max}=4$ we should be very close to the CBS limit, well within 1 mH accuracy in the total energy.

In the following we show the importance of being close to the CBS limit in QMC calculations obtained either by optimizing the Jastrow factor over the Slater determinant defined by the DFT Kohn-Sham molecular orbitals or by full optimizing both the Jastrow and the molecular orbitals with the method described in Ref. 5, starting from the former initial wave function. We indicate in the following the first wave function by J -DFT-WF, whereas the latter one will be denoted by J -OPT-WF.

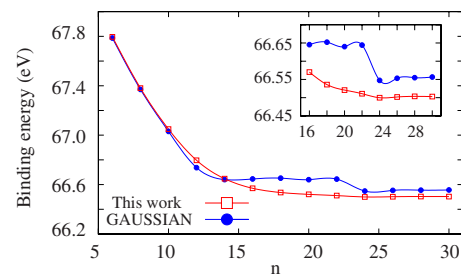


FIG. 5. (Color online) DFT atomization energy of the benzene molecule calculated by using a basis set containing only s and p atomic orbitals ($l_{max}=1$ limit). Results obtained by GAUSSIAN09 are also shown for comparison.

TABLE II. Total DFT energy for the benzene molecule as a function of the highest angular momentum of the atomic basis. Calculations were done with pseudopotentials (Ref. 14) both for the hydrogen and carbon atoms at the experimental equilibrium positions while for the hydrogen we have used a $3s2p$ basis.

L	Basis	C composition	Number of primitive Gaussian	Energy (H)
1	sp limit	$24s22p$	594	-37.4952567
2	spd limit	$24s22p10d$	894	-37.5357514
3	$spdf$ limit	$24s22p10d6f$	1146	-37.5400821
4	$spdfg$ limit	$24s22p10d6f2g$	1254	-37.5416815

A $4s3p2d$ ($1s1p$) uncontracted Gaussian basis set was used for expanding the Jastrow factor around each carbon (hydrogen) atom. Figure 6 shows the convergence of VMC total energy of the benzene molecule with J -DFT-WF, which an atomic basis used for the Slater determinant with $l_{\max}=1$. This picture shows that the presence of the Jastrow factor improves the convergence to the $n \rightarrow \infty$ limit. For instance the DFT total energy converges when the basis contains more than $24s$ and $22p$. Instead, by using the Jastrow factor, clear convergence is reached already for a $16s14p$ basis set. For fixed maximum angular momentum of the atomic basis l_{\max} in the Slater determinant, we have carried out VMC calculations of the total energy of the benzene molecule. As shown in Table III the total energy difference between the $l_{\max}=1$ and the $l_{\max}=2$ cases is about 0.75 (eV) while this difference for $l_{\max}=2$ and $l_{\max}=3$ shrinks to 0.25 (eV). Moreover our VMC results suggest that it is not necessary to add g orbital to the basis set, for an accuracy smaller than 0.005 (eV).

The VMC atomization energy of the benzene molecule within the J -DFT-WF for fixed l_{\max} is reported in Table IV. The estimated exact atomization energy of the benzene molecule is 59.33(3) (eV),²¹ by neglecting inner-shell correlation that we assume to be negligible with the pseudopotentials we have used.²² Therefore, by optimizing the Jastrow factor, one can get almost exact atomization energy as long as a large basis set is considered for the DFT Slater determinant.

One of the main outcome of our work is that the DFT Slater determinant is a very good input for QMC calculations, provided the basis used is sufficiently large. In fact by full optimization of both the Jastrow and the determinantal parts of the WF and by using a large basis for the Slater

determinant $24s22p10d6f$, the VMC total energy of the benzene molecule is $-37.6491(3)(H)$. Hence, the difference between the VMC total energy using the J -DFT-WF and the J -OPT-WF is very small 0.035 (eV) and this shows that, by optimizing the determinantal part of the WF, the total energy improves only by a small amount and does not appreciably change the atomization energy of benzene, from 59.37(4) (eV) to 59.41(3) (eV). Remarkably from a DFT-LDA atomization energy that is completely wrong by ~ 10 (eV), we can obtain an almost exact atomization energy using the J -DFT-WF wave function with the Kohn-Sham molecular orbitals obtained with the energetically poor DFT-LDA method.

A much different behavior is obtained when the wave function is fully optimized within a small basis set. Indeed, we have applied full optimization on the smallest basis set $6s4p$, and the VMC total energy using the J -OPT-WF is $-37.6384(5)(H)$, which is 1.12 (eV) below the corresponding J -DFT-WF energy. This energy gain is more than one order of magnitude larger than the one obtained in the previous case. Therefore we conclude that the Kohn-Sham molecular orbitals are very accurate only when a sufficiently large basis is used in the DFT calculation.

In this limit, in order to show the quality of our variational wave functions, we have carried out lattice regularized diffusion Monte Carlo (LRDMC) (Ref. 23) calculations using the J -DFT-WF and the J -OPT-WF. The LRDMC total and atomization energies of the benzene molecule are shown in Table V. Though the LRDMC improves the VMC total energy of the benzene molecule by about ≈ 1.7 (eV), the atomization energy remains unchanged within the statistical errors.

IV. CONCLUSION

We have introduced a very simple method to make accurate and systematically converging SCF calculations with lo-

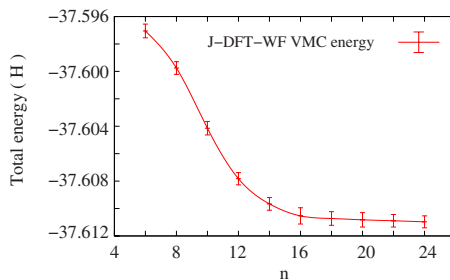


FIG. 6. (Color online) VMC total energy using the J -DFT-WF, defined in the text, for the benzene molecule as a function of the number of s and p orbitals. We have used DFT molecular orbital as a determinant part of trial wave function and only the Jastrow factor was optimized.

TABLE III. VMC total energy (H) of benzene molecule by using the J -DFT-WF defined in the text.

l	Basis	C composition	Energy (H)
1	sp limit	$24s22p$	$-37.6111(4)$
2	spd limit	$24s22p10d$	$-37.6386(4)$
3	$spdf$ limit	$24s22p10d6f$	$-37.6478(4)$
4	$spdfg$ limit	$24s22p10d6f2g$	$-37.6480(4)$

TABLE IV. VMC atomization energy of the benzene molecule obtained with the J -DFT-WF defined in the text.

l	Basis	C composition	Binding energy (eV)
1	sp limit	$24s22p$	58.38(4)
2	spd limit	$24s22p10d$	59.12(4)
3	$spdf$ limit	$24s22p10d6f$	59.37(4)
4	$spdfg$ limit	$24s22p10d6f2g$	59.37(4)

calized basis sets of increasing dimension. This work shows that the use of a large basis set may be extremely important for accurate calculations. It is possible that our method could be relevant also for defining more efficient electronic-structure packages that are free of any limitation about basis set dimension. Preliminary application of the method to periodic systems are also extremely encouraging,²⁴ because one can work also in this case with a localized basis set, with convergence properties similar to plane-wave DFT methods. For large extended systems the condition number of a GTO localized basis set increases quite rapidly with the system size but we have tested in silicon with a supercell containing up to 256 atoms (i.e., 1024 valence electrons) that our algorithm remains stable for fixed choice of the parameter $\epsilon_{mach} \approx 10^{-16}$ used to remove the singular directions. Although it is impossible to obtain the error of the finite basis used ($8s6p4d$ per atom) because the CBS limit is computationally too expensive for large number of electrons, by comparing our results with standard plane-wave methods it turns out that our accuracy should remain constant for the energy per atom. This is expected from general grounds, since for extended systems the condition number of a localized basis set, defined by a fixed number of orbitals per atom, should saturate in the infinite volume limit, when orbitals corresponding to atoms that are very far apart remain orthogonal,

TABLE V. LRDMC total and atomization energies of the benzene molecule obtained by the J -DFT-WF and the J -OPT-WF, described in the text.

	J -DFT-WF	J -OPT-WF
Total energy (H)	-37.7111(5)	-37.7128(4)
Binding energy (eV)	59.41(5)	59.45(4)

because they do not overlap. As we have already remarked before better accuracy—probably necessary for large extended systems when for instance the chemical accuracy in the total energy is required—can be in principle possible with much smaller ϵ_{mach} that can be used only with a more accurate arithmetic (e.g., quadruple precision).

Moreover we have shown that, for QMC applications, our method is extremely useful because only in the large basis set limit the output molecular orbitals of our new SCF calculation define an extremely accurate Slater determinant, that essentially, does not need to be optimized. This work also highlights a remarkable property of the DFT method, namely, that, rather surprisingly, the Kohn-Sham molecular orbitals are rather robust and stable in the large basis set limit, and do not seem to be very much sensitive to the accuracy of the functional used. In the benzene example for instance, the accuracy in the atomization energy with the LDA functional used was very poor with an error of about ≈ 10 eV, whereas when the same Kohn-Sham orbitals are used for standard QMC calculation, they provide almost optimal results, not only compatible with experiments but also stable against further optimization of the energy in presence of the Jastrow factor.

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$$v_S(r) = \operatorname{erfc}(kr)/r$$

and is used for computing efficiently the electron-ion and ion-ion Coulomb energies in the real-space mesh. Instead in the electron-electron Coulomb energy it is convenient to employ the

Fourier convolution with a slightly different Coulomb potential $\tilde{v}_c(q) = v_L(q) + \tilde{v}_S(q)$, where $\tilde{v}_S(q)$ is the discrete Fourier transform for the short-range part $\tilde{v}_S(q) = v \sum_{r_j \neq 0, r_j \in V} e^{-iqr} v_S(r) + C$. Indeed, it is convenient to use $\tilde{v}_c(q)$ in place of $v_c(q)$ in the Fourier convolution in order to be consistent with the calculation of the electron-ion and ion-ion contributions to the Coulomb energy. Moreover, analogously to the open system case, in order to obtain a much faster convergence the constant C is determined by requiring that

$$\tilde{v}_S(q=0) = \pi/k^2,$$

namely, the exact value of the integral for $n_x, n_y, n_z \rightarrow \infty$.

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