

Density functional calculation of many-electron systems in Cartesian coordinate grid

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Abstract A recently developed density functional method, within Hohenberg-Kohn-Sham framework, is used for faithful description of atoms, molecules in Cartesian coordinate grid, by using an LCAO-MO ansatz. Classical Coulomb potential is obtained by means of a Fourier convolution technique. All two-body potentials (including exchange-correlation (XC)) are constructed directly on real grid, while their corresponding matrix elements are computed from numerical integration. Detailed systematic investigation is made for a representative set of atoms/molecules through a number of properties like total energies, component energies, ionization energies, orbital energies, etc. Two nonlocal XC functionals (FT97 and PBE) are considered for pseudopotential calculation of 35 species while preliminary all-electron results are reported for 6 atoms using the LDA XC density functional. Comparison with literature results, wherever possible, exhibits near-complete agreement. This offers a simple efficient route towards accurate reliable calculation of many-electron systems in the Cartesian grid. Future prospect of this method is also discussed.

Keywords Density functional theory · Exchange correlation functional · Cartesian grid

1 Introduction

Within density functional theory (DFT), ground-state energy of a many-electron system is conveniently divided into specific components as follows:

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$$E[\rho(\mathbf{r})] = T_{ni}[\rho(\mathbf{r})] + V_{ne}[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})] + \Delta T[\rho(\mathbf{r})] + \Delta V_{ee}[\rho(\mathbf{r})] \quad (1)$$

Here, from left to right, the terms in right-hand side denote kinetic energy of the non-interacting electrons, nuclear-electron attraction, classical electron-electron repulsion, *correction* to kinetic energy arising out of the interacting nature of electrons, and *all* non-classical corrections to the electron repulsion energy (including exchange and correlation), respectively. Now, using an orbital expression for density, above equation may be recast as,

$$E[\rho(\mathbf{r})] = \sum_i^N \left(\left\langle \psi_i \left| -\frac{1}{2} \nabla_i^2 \right| \psi_i \right\rangle - \left\langle \psi_i \left| \sum_k^M \frac{Z_k}{|\mathbf{r}_i - \mathbf{r}_k|} \right| \psi_i \right\rangle + \left\langle \psi_i \left| \frac{1}{2} \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}_i - \mathbf{r}'|} d\mathbf{r}' \right| \psi_i \right\rangle \right) + E_{xc}[\rho(\mathbf{r})] \quad (2)$$

where N, M denote number of electrons and nuclei respectively, whereas density of a Slater determinantal wave function (exact for a non-interacting system) is simply $\rho = \sum_i^N \langle \psi_i | \psi_i \rangle$.

As in the Hartree-Fock (HF) case, Kohn-Sham (KS) DFT equations also cannot be solved exactly and recourse must be taken to approximations. However, the required iterative process of solving KS equations is conceptually very similar to that encountered for solving HF equations. Two major routes have been explored for practical solution of a molecular KS equation. The *real-space* method [1–4] involves an iterative mechanism for a discretized KS equation on a real mesh using either of finite-difference, finite-element or wavelet technique. Typically this *whole* molecular grid belongs to either uniform or refined uniform grids. Some important advantages of this method are that (a) grid-based matrix representation offers highly structured banded matrices (b) potential operator is diagonal in coordinate space whereas Laplacian operator is nearly local (c) they are easily amenable to the so-called linear scaling methods. Usually these schemes require exceedingly large grid points to capture the complete physical system of interest, which is essential to deliver physically and chemically acceptable results. However with the introduction of higher order and multi-grid techniques, grid points could be considerably cut down without sacrificing much accuracy.

The other alternative, which is more often used these days, relies on an expansion of eigenfunctions in terms of some suitable *basis functions* such as Slater or Gaussian type functions (GTF), plane waves, numerical functions, augmented plane waves, linear muffin-tin orbitals, etc. Of these, GTFs are the most favorites, for they provide easy analytic routes towards relevant multi-center integrals,

$$\psi_i(\mathbf{r}) = \sum_{\mu=1}^K C_{\mu i} \chi_{\mu}(\mathbf{r}), \quad i = 1, 2, \dots, K \quad (3)$$

A central problem common to almost all DFT approaches is that of obtaining the classical Coulomb (V_c) and XC (V_{xc}) potentials from electron density. In general, these cannot be obtained in any analytic form, and hence numerical treatments are necessary for evaluation of subsequent matrix elements. This is also true for energy

integrals associated with XC energy; $E_{xc}[\rho(\mathbf{r})] = \int \epsilon_{xc}[\rho(\mathbf{r})] d\mathbf{r}$. In order to circumvent this problem, in some molecular DFT implementations (see, [5,6], for example), electron density and XC potentials are *also* expanded in some auxiliary Gaussian bases viz., $\rho(\mathbf{r}) \simeq \tilde{\rho}(\mathbf{r}) = \sum_i^{N_\rho} C_i^\rho f_i^\rho(\mathbf{r})$, $V_{xc}(\mathbf{r}) \simeq \tilde{V}_{xc}(\mathbf{r}) = \sum_j^{N_{xc}} C_j^{xc} f_j^{xc}(\mathbf{r})$, following some fitting procedure (so called discrete variational method) [7–11], in addition to an MO expansion. This facilitates an N^3 scaling. Later, robust variational fitting that corrects a target function to first order in fitting error has been developed for a variety of problems, such as Coulomb potential, resolution of identity methods, KS potential, MP2 methods, first-principles molecular dynamics, etc. [12–14].

A vast majority of modern DFT implementations employ the so-called atom-centered grid (ACG), pioneered by Becke [15], where a molecular grid is conveniently described in terms of some suitable 3D quadratures. The basic idea is to decompose real molecular space into overlapping atomic regions which are described by fuzzy Voronoi polyhedra. These discrete mono-centric atomic integrals can be individually approximated using some standard numerical techniques. Finally, summing these contributions with appropriate weight functions leads to the desired molecular integration result. The atomic grid constitutes of a tensor product between radial part, defined in terms of some quadrature formulas such as Gauss-Chebyshev, Gaussian, Euler-McLaurin, multi-exponential numerical, etc., [16–22] and Lebedev angular quadratures (order as high as 131 has been reported, although usually much lower orders suffice; 59th order is the one most frequently used) [23–25]. Many variants of original Becke integration scheme have been proposed thereafter, mainly to prune away some extraneous grid points which could be quite beneficial. Recently Becke's multicenter grid expansion for orbitals and potentials has also been used in the context of fully numerical HF equation, without basis-set error [26]. Attempts were also made to perform such integrations by dividing whole space and invoking product Gauss rule to complete the subsequent integrations [27]. In a variational integration scheme, on the other hand, molecular space has been categorized into three different regions such as atomic spheres, excluded cubic region and interstitial parallelepiped [28]. In the Fourier transform Coulomb and multiresolution technique, Cartesian coordinate grid (CCG) was used in addition to ACG [29,30]; former divides Gaussian shell pairs into "smooth" and "sharp" categories on the basis of exponents while latter connects ACG and CCG by means of a divided-difference polynomial interpolation to translate density and gradients from latter to former. An accurate multiresolution solver has been developed for atoms and molecules within KS DFT using multiwavelet bases with good success [31–34]. It may be noted that as alternative to the atom-center-based decomposition of the grid, *whole* molecular integration grids based on Smolyak-type sparse-tensor products, have been prescribed for accurate numerical calculation of molecules. For more details on the whole molecular grid, consult [35–37] and the references therein.

Recently, DFT calculations [38–40] of atoms and molecules have been performed using linear combination of Gaussian-type-orbital-expansion for KS molecular orbitals within CCG only. While no auxiliary basis set was invoked for charge density

or XC potentials, localized atom-centered basis functions, MOs, electron density as well as classical two-electron Hartree and non-classical XC potentials were built on 3D real grid directly. The Coulomb potential was obtained from a Fourier convolution technique, involving a combination of FFT and inverse FFT, accurately and efficiently [41,42]. Analytical one-electron Hay-Wadt-type effective core potentials, made of a sum of GTFs, were used to represent the inert core electrons while energy-optimized truncated Gaussian bases were used for valence electrons [43,44]. Detailed results were presented [38–40] including total energy, energy components, orbital energy, potential energy curve, atomization energy for local density-approximated (LDA) [45] and non-local Becke exchange [46]+Lee-Yang-Parr correlation [47], to assess the performance and accuracy of this newly proposed method. Pseudopotential calculations on about 5 atoms and 53 molecules for these above quantities produced practically identical results as those obtained from the widely used GAMESS quantum chemistry program [48], which, of course, works in ACG. It is well-known that although LDA and BLYP functionals perform satisfactorily for many physical and chemical processes, in many occasions they behave rather poorly and clearly there is genuine need for better functionals. In fact, construction of accurate, proper XC functionals has been a very active, fertile area of research ever since the inception of KS formalism. The literature is vast and it is an ongoing process. Some of the other functionals in recent use are generalized gradient expansion, hybrid functionals, meta functionals, orbital-dependent functionals, etc., (see, e.g., [49] for a lucid review). In this article, we employ two of them, viz., Filatov-Thiel (FT97) [50, 51] and PBE [52] (for 8 atoms, 27 molecules), in order to extend the scope and applicability of this approach. These functionals have been used in many applications of many-electron systems with reasonably good success. Also one of our main objectives to develop such a full CCG-based DFT procedure lies in the hope that LCAO-MO-DFT, which has enjoyed such a conspicuous success for enormous application for electronic structure of atoms/molecules in static case during past several decades, might also be equally successful for real-time dynamics studies (especially atoms/molecules in presence of an external field, such as a strong laser field, etc.) within the broad rubric of time-dependent (TD) DFT. Although considerable theoretical progress has been made for real-space dynamical studies of atoms/molecules under strong fields within TDDFT (see, for example, [53], for a review), several non-trivial problems are encountered for arbitrary atomic/molecular system. Extension in these cases is not straightforward, for they pose considerable challenge. On the other hand, extension of these above-mentioned LCAO-MO-based DFT approaches within ACG is quite difficult in the TD domain. In order to proceed further in that direction, here, for the first time, we report full all-electron calculation of several atoms using the basis set method, completely in CCG. This constitutes an essential first step (the “structure” part) much needed for real-time TDDFT studies. To this end, total energies, component energies, orbital energies as well as HOMO energies from these full calculations are compared systematically with reference literature values. Section 2 gives a brief overview of the methodology used; discussion on our results are given in Sect. 3, while we end with a few concluding remarks in Sect. 4.

2 Methodology

The method employed in this work has been presented before [38–40] in some detail. Hence will not be repeated here; only essential details are given. Unless otherwise mentioned, atomic units implied henceforth.

In KS DFT, the problem of calculating total ground-state electronic energy of a many-electron system is transformed into solving the following single-particle KS equation,

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_h(\mathbf{r}) + v_{xc}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (4)$$

Here v_{ext} signifies the external potential in which electrons move, containing an electrostatic potential due to the presence of nuclei, but may also include other terms (in present occasion, none); v_h denotes classical Coulomb potential arising because of the electron distribution; and finally v_{xc} corresponds to a multiplicative XC potential that depends on electron density, but not on wave functions explicitly.

As already mentioned, KS MOs are built from localized Gaussian type basis functions as in Eq. (3). The LCAO-MO approach is quite efficient; for it can give very accurate results and also it provides basis for creation of new methods such as order-N, Green's function approaches, etc. Note, full self-consistent DFT procedure requires specification of basis functions; therefore a price is to be paid for efficiency in terms of loss of generality (in contrast to, for example, a plane wave method, where "one basis fits all" philosophy works). Several important factors must be considered for building and choosing basis functions for a particular problem; two most important of them being (i) reduction of number of functions and (ii) ease of computation of relevant integrals. The electron density is described in terms of basis functions and corresponding one-body density matrix P as,

$$\rho(\mathbf{r}) = \sum_{i=1}^N \sum_{\mu=1}^K \sum_{\nu=1}^K C_{\mu i} C_{\nu i} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) = \sum_{\mu} \sum_{\nu} P_{\mu\nu} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}) \quad (5)$$

where $P_{\mu\nu}$ denotes an element of the density matrix. In a spin-unrestricted formalism, $\rho(\mathbf{r}) = \rho^{\alpha}(\mathbf{r}) + \rho^{\beta}(\mathbf{r})$, $P = P^{\alpha} + P^{\beta}$, and KS SCF wave function satisfies the following set of equations, which are reminiscent of Pople-Nesbet equations in HF theory,

$$F^{\alpha} C^{\alpha} = S C^{\alpha} \epsilon^{\alpha}, \quad \text{and} \quad F^{\beta} C^{\beta} = S C^{\beta} \epsilon^{\beta} \quad (6)$$

with the orthonormality conditions,

$$(C^{\alpha})^{\dagger} S C^{\alpha} = I, \quad \text{and} \quad (C^{\beta})^{\dagger} S C^{\beta} = I \quad (7)$$

Here C^{α} , C^{β} are matrices containing MO coefficients, S is the atomic overlap matrix, and ϵ^{α} , ϵ^{β} are diagonal matrices of orbital eigenvalues. F^{α} , F^{β} are KS matrices corresponding to α , β spins respectively, having matrix elements as,

$$F_{\mu\nu}^{\alpha} = \frac{\partial E_{KS}}{\partial P_{\mu\nu}^{\alpha}} = H_{\mu\nu}^{\text{core}} + J_{\mu\nu} + F_{\mu\nu}^{XC\alpha}, \quad \text{and} \quad F_{\mu\nu}^{\beta} = \frac{\partial E_{KS}}{\partial P_{\mu\nu}^{\beta}} = H_{\mu\nu}^{\text{core}} + J_{\mu\nu} + F_{\mu\nu}^{XC\beta} \quad (8)$$

Here $H_{\mu\nu}^{\text{core}}$ represents the bare-nucleus Hamiltonian matrix that accounts for one-electron energies, including contributions from kinetic energy plus nuclear-electron attraction. $J_{\mu\nu}$ term refers to matrices from classical Coulomb repulsion whereas the third term arises from non-classical XC effects. Last one remains the most difficult and challenging part of the whole SCF process.

All one-electron integrals including overlap, kinetic-energy, nuclear-electron attraction as well as pseudopotential matrix elements are identical to those found in HF theory in Cartesian Gaussian functions and are generated by standard recursion algorithms. Here we employ angular-momentum dependent pseudopotentials as those from [43,44]. Classical Hartree potential, for finite systems is most simply and crudely computed by means of direct numerical integration. However, this shows poor performance in many occasions and typically feasible only for relatively smaller systems. One important successful route is through the solution of corresponding Poisson equation by means of various techniques such as multigrid or a combination of multigrid and wavelet methods (see, for example, [54,55] and references therein). Here the classical electrostatic potential is obtained in the grid, by an alternate Fourier convolution technique [41,42], shown to be quite accurate and efficient for molecular modeling. This relies on a Ewald summation type decomposition of $1/r$ in terms of a pair of short-range (in terms of complimentary error function) and long-range (in terms of error function) contributions; former can be obtained analytically whereas the latter is computed directly from FFT of real-space values.

$$\begin{aligned} \rho(\mathbf{k}_g) &= \text{FFT}\{\rho(\mathbf{r}_g)\} \\ v_H(\mathbf{r}_g) &= \text{FFT}^{-1}\{v_H^c(\mathbf{k}_g) \rho(\mathbf{k}_g)\} \end{aligned} \quad (9)$$

Here $\rho(\mathbf{k}_g)$, the Fourier integral of density, is easily calculated from standard FFT, while $v_H^c(\mathbf{k}_g)$ signifies that of Coulomb interaction kernel in the grid which requires caution.

The nonlocal XC functionals of [50–52] are used in this work; while for LDA calculations homogeneous electron-gas correlation [45] is used. The gradient-dependent functionals are handled by using a finite-orbital expansion method [56], which allows one to bypass the calculation of difficult density Hessians. In the end, XC matrix elements are evaluated as,

$$F_{\mu\nu}^{XC\alpha} = \int \left[\frac{\partial f}{\partial \rho_{\alpha}} \chi_{\mu} \chi_{\nu} + \left(2 \frac{\partial f}{\partial \gamma_{\alpha\alpha}} \nabla \rho_{\alpha} + \frac{\partial f}{\partial \gamma_{\alpha\beta}} \nabla \rho_{\beta} \right) \cdot \nabla (\chi_{\mu} \chi_{\nu}) \right] d\mathbf{r} \quad (10)$$

where $\gamma_{\alpha\alpha} = |\nabla \rho_{\alpha}|^2$, $\gamma_{\alpha\beta} = \nabla \rho_{\alpha} \cdot \nabla \rho_{\beta}$, $\gamma_{\beta\beta} = |\nabla \rho_{\beta}|^2$. The advantage is that f is a function *only* of local quantities ρ_{α} , ρ_{β} and their gradients. Non-local functionals are implemented using the Density Functional Repository program [57]. There is no direct analytic route to evaluate two-electron matrix elements. Present work uses numerical

integration for these in a 3D CCG covering a cubic box. Resulting matrix-eigenvalue problem is solved accurately and efficiently by means of standard LAPACK library package [58]. Self-consistent solutions are obtained by imposing a tolerance of 10^{-6} for energy and eigenvalues whereas 10^{-5} for potential.

3 Results and discussion

At first, we show FT97 and PBE results for 8 atoms and 27 molecules in Table 1 within the pseudopotential framework. Throughout the whole article, molecular geometries are used from those in NIST database [59]. We report non-relativistic ground-state total, kinetic and potential energies for all these species using the effective core potential of [43, 44]. For sake of completeness, our integrated electron density is also given which can sometimes work as a rough indicator of accuracy and quality attained in a given calculation. Several grid parameters were tried to check convergence, as in previous papers [38, 39]. However as expected and observed, they produced very similar results in the present occasion as well; discrepancies were rather very small from one set to other. In the end, $N_r = 128$, $h_r = 0.3$ seemed to be a very good reasonable choice, in keeping with our observations in [39]. In contrast to our earlier works, the GAMESS theoretical results could not be reported in this case, as results from these functionals are not available there. Excepting the lone case of Na, in all other 34 cases, FT97 total energies are found to be consistently lower than PBE values. Keeping in mind the performance of our results for LDA and BLYP results in previous occasions, one can safely conclude that our current results are also equally accurate and trustworthy.

Now, Table 2 offers a comparison of our calculated ionization energies ($-\epsilon_{\text{HOMO}}$) with literature results, for all the 27 molecules of Table 1. In addition to the aforementioned FT97 and PBE results, here we have also appended the BLYP results from [40], for sake of comparison. Out of these, experimental values are not available for 6 species, and wherever possible they are adopted from [60]. Three ionization energies, although quantitatively different from each other as expected, produce similar qualitative results. However all 3 values are rather quite low compared to the experimental data. As is well-known, a number of factors such as basis set, XC functional, relativistic effects, etc., are responsible for this discrepancy. This does not, however, interfere with the main objective of this work directly and may be taken up later in our future studies. It is worth mentioning here that, none of these 3 functionals lead to ionization energies for these molecules as good (or even close to) as those from LBVWN (reported in [40]). For a moderate set of atoms and molecules, this latter XC combination showed significant improvements in HOMO energies over LDA, BLYP results and now FT97, PBE functionals as well.

So far all the results presented using our method employed some sort of effective core potentials to incorporate the effects of frozen core electrons; no investigation has been made for the so-called “full” all-electron calculations. Although pseudopotential studies are advantageous for larger systems, especially those containing one or more heavier atoms where full calculations could be expensive, latter are very desirable otherwise, for they can provide more detailed and also more accurate results. Thus

Table 1 Kinetic (T), potential (V), total (E) energies and N for several atoms and molecules

System	$\langle T \rangle$		$-\langle V \rangle$		$-\langle E \rangle$		N	
	PBE	FT97	PBE	FT97	PBE	FT97	PBE	FT97
Na	0.06795	0.06966	0.25344	0.25482	0.18548	0.18516	0.99999	0.99999
Mg	0.24078	0.24422	1.05699	1.07027	0.81621	0.82605	1.99999	1.99999
Na ₂	0.13774	0.14152	0.52488	0.53711	0.38714	0.39559	1.99999	1.99999
NaH	0.52183	0.52627	1.26204	1.27956	0.74020	0.75329	1.99999	1.99999
Si	1.33042	1.37824	5.09142	5.15100	3.76099	3.77276	3.99999	3.99999
Mg ₂	0.48713	0.49602	2.12361	2.14993	1.63648	1.65391	3.99999	3.99999
AlH	1.16864	1.19789	3.69496	3.74500	2.52631	2.54710	3.99999	3.99999
MgH ₂	1.24003	1.27593	3.20349	3.26711	1.96346	1.99118	3.99999	3.99999
P	2.32561	2.39816	8.74650	8.83346	6.42089	6.43530	4.99999	4.99999
As	2.04560	2.10981	8.11083	8.18445	6.06524	6.07465	4.99999	4.99999
SiH	1.87657	1.92371	6.23753	6.30523	4.36096	4.38152	4.99999	4.99999
AlH ₂	1.70807	1.75842	4.80730	4.87927	3.09923	3.12085	4.99999	4.99999
S	3.63873	3.70741	13.66799	13.75933	10.02926	10.05193	6.00000	6.00000
Al ₂	1.32292	1.34896	5.20904	5.25881	3.88612	3.90985	5.99999	5.99999
PH	2.88362	2.95298	9.90110	9.99256	7.01748	7.03959	5.99999	5.99999
SiH ₂	2.42339	2.47351	7.39314	7.47217	4.96975	4.99866	5.99999	5.99999
Cl	5.50351	5.56491	20.38372	20.47315	14.88021	14.90824	7.00000	7.00000
Br	4.17153	4.22828	17.29168	17.37615	13.12015	13.14787	6.99999	6.99999
SH	4.22535	4.28816	14.86811	14.95915	10.64276	10.67100	7.00000	7.00000
HSe	3.55021	3.60577	13.32383	13.40808	9.77362	9.80231	6.99999	6.99999
PH ₂	3.43226	3.49937	11.05733	11.15375	7.62507	7.65438	6.99999	6.99999
SiH ₃	3.03138	3.09386	8.54321	8.63382	5.51184	5.53996	6.99999	6.99999
HBr	4.73573	4.79470	18.47807	18.57128	13.74234	13.77657	8.00000	8.00000
HI	3.59156	3.64696	15.55969	15.64856	11.96813	12.00160	7.99999	7.99999
PH ₃	3.99643	4.06590	12.24024	12.34634	8.24382	8.28044	7.99999	7.99999
H ₂ S	4.83030	4.89575	16.09889	16.19906	11.26859	11.30331	7.99999	7.99999
H ₂ Se	4.10439	4.16513	14.49460	14.59143	10.39021	10.42631	8.00000	8.00000
SiH ₄	3.53302	3.60707	9.75741	9.86882	6.22438	6.26175	7.99999	7.99999
P ₂	4.74887	4.80387	17.72258	17.81522	12.97371	13.01135	9.99999	9.99999
S ₂	7.51586	7.59269	27.64063	27.76097	20.12477	20.16828	12.00000	12.00000
Se ₂	6.14886	6.21184	24.55724	24.66671	18.40838	18.45487	11.99999	11.99999
Br ₂	8.47065	8.55429	34.76026	34.89602	26.28961	26.34173	13.99999	13.99999
H ₂ S ₂	8.65115	8.74098	29.99986	30.14139	21.34871	21.40041	13.99999	13.99999
S ₃	11.36056	11.45542	41.58894	41.74371	30.22838	30.28829	17.99999	17.99999
P ₄	9.95263	10.05211	35.89638	36.05954	25.94375	26.00742	19.99999	19.99999

PBE and FT97 results are given in a.u. See text for details

Table 2 Comparison of $-\epsilon_{\text{HOMO}}$ energies (in a.u.) for some molecules calculated using BLYP, FT97 and PBE XC functionals, with literature data

Molecule	$-\epsilon_{\text{HOMO}}$				Molecule	$-\epsilon_{\text{HOMO}}$			
	BLYP	FT97	PBE	Expt.		BLYP	FT97	PBE	Expt.
Na ₂	0.1002	0.0862	0.0952	0.1798	NaH	0.1421	0.1231	0.1324	–
Mg ₂	0.1530	0.1293	0.1395	–	AlH	0.1715	0.1362	0.1521	–
MgH ₂	0.2221	0.1857	0.2024	–	SiH	0.1597	0.1305	0.1514	0.2900
AlH ₂	0.1631	0.1253	0.1468	–	Al ₂	0.1400	0.1161	0.1318	0.1984
PH	0.2133	0.1786	0.2012	0.3730	SiH ₂	0.2027	0.1619	0.1808	0.3278
SH	0.2174	0.1809	0.1994	0.3830	HSe	0.2057	0.1746	0.1903	0.3618
PH ₂	0.2111	0.1741	0.1970	0.3610	SiH ₃	0.1969	0.1590	0.1825	0.2990
HBr	0.2603	0.2249	0.2439	0.4292	HI	0.2432	0.2122	0.2302	0.3817
PH ₃	0.2287	0.1854	0.2054	0.3627	H ₂ S	0.2190	0.1815	0.2006	0.3843
H ₂ Se	0.2075	0.1731	0.1916	0.3635	SiH ₄	0.3156	0.2702	0.2919	0.4042
P ₂	0.2526	0.2206	0.2360	0.3870	S ₂	0.2023	0.1594	0.1781	0.3438
Se ₂	0.1951	0.1576	0.1749	0.3160	Br ₂	0.2451	0.2115	0.2285	0.3865
H ₂ S ₂	0.2288	0.1928	0.2103	0.3418	S ₃	0.2294	0.1985	0.2143	–
P ₄	0.2575	0.2369	0.2525	0.3432	–	–	–	–	–

BLYP and experimental results are taken from refs. [40] and [60] respectively. See text for details

they add valuable insights into a particular problem. As long as the cost accuracy ratio permits, these are the preferred choices for most chemical and physical studies. In an attempt to deal with such situations, as a very first step, in Table 3, some representative preliminary all-electron results are given for a set of 6 atoms using this approach to assess its level of performance and effectiveness in the said domain. For all these, we use LDA XC potential, STO-3G basis set and $N_r = 128$, $h_r = 0.3$. We are not aware of any other attempts where such studies have been made within the LCAO framework, using CCG only. Besides the point mentioned above in this paragraph, there are other important motivations for this case study, which have been elaborated in Section I. These are all open-shell systems and a thorough comparison with the GAMESS program is made for all of them, using same basis set as well as same XC functional. Following quantities are reported: kinetic energy $\langle T \rangle$, nuclear-electron attraction energy $\langle V_{ne} \rangle$, classical Hartree energy $\langle E_h \rangle$, exchange energy $\langle E_x \rangle$, correlation energy $\langle E_c \rangle$, two-electron potential energy $\langle V_{ee} \rangle$, total potential energy $\langle V \rangle$, total electronic energy $\langle E \rangle$, total integrated electron density N as well as all the α - and β -spin orbital energies. Note that literature results employ Euler-McLaurin and Gauss-Legendre quadratures for radial and angular integrations respectively. The default grid option is used for all these reference results. Individual Coulomb repulsion and XC energies from literature could not be cited as GAMESS output does not report those. Quite clearly, for all these quantities, agreement with literature results is excellent (very similar accuracy, as we observed in the pseudopotential case before); present results practically coincide with the reference values. It is well-known that STO-3G basis set employed here is not a very accurate one, and used here only for the demon-

Table 3 Energy components as well orbital energies for several atoms using Cartesian grid. All-electron calculations with LDA XC functionals using STO-3G basis set are given along with those obtained from reference GAMESS program

Quantity	Li		Be		B	
	This work	Ref. [48]	This work	Ref. [48]	This work	Ref. [48]
$\langle T \rangle$	7.38213	7.38212	14.84418	14.84419	25.30018	25.30018
$\langle V^{ne} \rangle$	-17.11549	-17.11549	-34.07189	-34.07189	-58.14361	-58.14361
$\langle E_h \rangle$	4.24103		7.64382		12.66071	
$\langle E_x \rangle$	-1.57407		-2.40486		-3.47888	
$\langle E_c \rangle$	-0.15489		-0.23242		-0.30248	
$\langle V^{ee} \rangle$	2.51207	2.51207	5.00654	5.00656	8.87935	8.87936
$\langle V \rangle$	-14.60343	-14.60342	-29.06535	-29.06533	-49.26426	-49.26425
$\langle E \rangle$	-7.22130	-7.22130	-14.22116	-14.22114	-23.96408	-23.96406
N	2.99999	2.99999	3.99999	3.99999	4.99999	4.99999
ϵ_{1s}^α	-1.7289	-1.7289	-3.5755	-3.5754	-6.0874	-6.0873
ϵ_{2s}^α	-0.0815	-0.0815	-0.1288	-0.1288	-0.2053	-0.2053
$\epsilon_{2p_x}^\alpha$					0.0224	0.0224
ϵ_{1s}^β	-1.7139	-1.7139	-3.5755	-3.5754	-6.0722	-6.0721
ϵ_{2s}^β			-0.1288	-0.1288	-0.1578	-0.1578
	C		N		O	
	This work	Ref. [48]	This work	Ref. [48]	This work	Ref. [48]
$\langle T \rangle$	37.92456	37.92456	53.66407	53.66407	73.44497	73.44497
$\langle V^{ne} \rangle$	-88.64983	-88.64983	-127.32649	-127.32649	-176.32432	-176.32432
$\langle E_h \rangle$	18.78009		26.67740		37.46227	
$\langle E_x \rangle$	-4.64014		-5.98724		-7.49030	
$\langle E_c \rangle$	-0.36805		-0.43478		-0.54395	
$\langle V^{ee} \rangle$	13.77190		20.25538	20.25536	29.42801	29.42799
$\langle V \rangle$	-74.87793		-107.07111	-107.07113	-146.89631	-146.89634
$\langle E \rangle$	-36.95337	-36.95339	-53.40704	-53.40701	-73.45134	-73.45137
N	5.99999	5.99999	6.99999	6.99999	7.99999	7.99999
ϵ_{1s}^α	-9.4882	-9.4879	-13.6312	-13.6311	-18.3331	-18.3330
ϵ_{2s}^α	-0.3970	-0.3970	-0.6152	-0.6153	-0.7538	-0.7537
$\epsilon_{2p_x}^\alpha$	-0.0675	-0.0676	-0.1671	-0.1672	-0.1941	-0.1942
$\epsilon_{2p_y}^\alpha$	-0.0648	-0.0649	-0.1671	-0.1672	-0.1941	-0.1942
$\epsilon_{2p_z}^\alpha$			-0.1671	-0.1672	-0.1085	-0.1084
ϵ_{1s}^β	-9.4573	-9.4572	-13.5837	-13.5836	-18.2972	-18.2971
ϵ_{2s}^β	-0.2923	-0.2924	-0.4449	-0.4450	-0.6301	-0.6302
$\epsilon_{2p_x}^\beta$					-0.0378	-0.0379

See text for details

stration purposes. Certainly better basis sets needs to be used for realistic calculations. These, as well as the molecular case, may be considered in future communications. However, the main motivation, at this stage, was to establish the validity and feasibility of this approach in the context of full electronic structure calculation of many-electron systems.

4 Concluding remarks

Many-electron systems have been studied by LCAO-MO-DFT in CCG. Both atoms and molecules (small as well as medium) were considered. Results have been presented for pseudopotential and all-electron calculations. For the former we employed FT97 and PBE XC functionals, as a follow-up of our previous work in this direction which further consolidates the success of this approach. For the latter, exploratory preliminary results were given using some rudimentary basis set within the homogeneous-electron gas approximation; this further extends the scope and applicability of the current scheme. The basis set, MOs, electron density and various potentials were generated in a CCG encapsulating a cubic box. Hartree potential was conveniently computed via a Fourier convolution method. Two-body matrix elements were obtained by direct numerical integration. Detailed comparison has been made with literature results, wherever possible, for a variety of quantities such as total energy, component energy, orbital energy, ionization energy, etc. Agreement has been extremely good; present results are almost indistinguishable from reference ACG-based DFT values (out of 6 atoms, largest absolute deviation in total energy from literature values is 0.00003 a.u. only). However, it would be necessary to incorporate better and more practical basis sets as well as other XC functionals (such as the simpler, accurate OPTX and OPTC functionals [61–63]) for more meaningful physical, chemical applications. Lately, suggestion has been made that the Coulomb potential in a molecular problem could be obtained by solution of the Poisson equation by generalizing the ideas used for a confined interacting model system embedded in a box [64]. It may be worthwhile to adopt such a scheme in the context of present approach as well, and may be taken up as a future work. In conclusion, this present study confirms the fact that electronic structure calculation of many-electron systems can be performed within LCAO-MO-based DFT, using Gaussian basis sets, very accurately and efficiently through CCG, offering virtually same accuracy as ACG.

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