**Asian Journal of Chemical Sciences**

**3(2): 1-9, 2017; Article no.AJOCS.34565**
*ISSN: 2456-7795*

# Ground State Electronic Energy and Ionization Energy of Atoms: Basis Free Density Functional Calculation

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***Author's contribution***

*The sole author designed, analyzed and interpreted and prepared the manuscript.*

***Article Information***

DOI: 10.9734/AJOCS/2017/34565
*Editor(s):*
(1) Zygadlo Julio Alberto, Professor of Chemistry, National University of Cordoba, Argentina.
*Reviewers:*
(1) Heinrich Ehrlich, Lomonosov Moscow State University, Russia.
(2) A.K. Bhatia, USA.
(3) Subramaniam Jahanadan, Labuan Matriculation College, Malaysia.
Complete Peer review History: http://www.sciencedomain.org/review-history/20723

***Original Research Article***

***Received 31$^{st}$ May 2017***
***Accepted 2$^{nd}$ July 2017***
***Published 29$^{th}$ August 2017***

## ABSTRACT

A new energy functional is proposed for basis free Density Functional Theory (DFT) calculation. Electronic density is calculated using atomic radii considering the atom as spherical. Ground-state electronic energies and ionization energies of atoms with $Z = 1 - 120$ are presented. Energy functional is partitioned numerically. Thus, this method may be termed as partitioned classical density functional theory (PCDFT). It is demonstrated that one can define an energy functional *solely* on the classical grounds which reduce the computational cost of storage and time. Calculated electronic energies and ionization energies are in reasonably good agreement with the quantum mechanical results of Relativistic Hartree Fock (RHF) method in the large basis set. Total energies and ionization energies show mean absolute percent deviations as $0.887$ and $8.73$ respectively. Given the fact that it is a simple, basis-set free, easy to implementable, one-step method, it could be useful for larger systems.

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*Keywords: Energy functional; PCDFT; Ionization energy; Atomic property.*

**PACS :** 03.65.w, 31.15.p, 32.10.f.

# 1 INTRODUCTION

Present day computational chemistry is constituted of a host of sophisticated, powerful and accurate methods. Majority of these are *traditional* wave function-based methods, such as Hartree Fock (HF)[1], Configuration Interaction (CI)[1], Perturbation theory (PT)[1, 2], Coupled Cluster (CC) theory [2, 3, 4], etc. Alternatively, there are density-based methods like Density functional theory (DFT) [5, 6]which employs single-particle density as the key element. Within this broad classification there are several subdivisions. Some of these are further divided into single-reference and multi-reference (MR) approaches. MR CC methods are again divided into state-selective approach, which is a single-root method, and multi-root approach involving an effective Hamiltonian within the Bloch method. There are two different routes in effective Hamiltonian methods; *viz.*, Hilbert space MRCC [7] and Fock space MRCC [3]. There is another class of CC method named Equation of Motion coupled cluster [8]. CC methods are very accurate and useful for small molecules, but computationally challenging for large systems. Same is true for other ab-initio methods as well. Full CI is considered as an exact method within a given basis set; however, its implementation is restricted due to computational constraints. Many interesting innovative ideas have been put forth in the past two decades to optimize the computational requirement and the process still continues.

Density-based methods, on the other hand, employs the 3D, physically realizable, single-particle electron density in contrast to the complex-valued wave function of $3N$ space and $N$ spin coordinates. Today's electronic structure calculation of materials is largely dominated by DFT, primarily due to its ability to account for the electron correlation effects in a transparent and accurate manner. This is done through the introduction of a fictitious non-interacting system having the same ground-state density of the *real* system concerned. The most challenging part of the problem remains in finding the elusive, yet-to-be-found, all-important exchange correlation (XC) energy density functional, whose exact form is unknown as yet and must be approximated in practice. For smaller systems, the electron correlation effects are conveniently and accurately described by CC, CI, MP etc. However, for complicated larger systems, DFT has an edge over these methods, due to its unique ability to strike a balance between quantitative accuracy and efficient computational resource in conjunction with readily interpretable conceptual simplicity.

This work relates the energy of a many-electron atom directly to the number of electrons and geometry of the system without any basis-set expansion. To this end, explicit expressions for energy and ionization energy of atoms are given in terms of the total number of electrons and radius of the corresponding atom. Investigation on 120 atoms in the periodic table shows that, obtained results are in agreement with non-relativistic HF and numerical relativistic Dirac Fock results [9]. It does not involve any computational complexity (such as no basis-set dependence, no self-consistency, etc.) and very easily implemented for the system at hand, irrespective of the number of electrons.

In section II, we present an account of the methodology for atomic properties. Section III gives a comparison of our results with the accurate quantum mechanical ones available in the literature. Merits and demerits of this approach are also discussed in this section. Finally, section IV concludes with a few pertinent remarks.

# 2 THEORY

Practical application of the HF and HF-based methods such as CC, CI, MP or even the DFT methods usually employs a linear combination of the atomic orbitals as basis to expand the molecular orbitals. Apart from other factors, partly these atomic orbitals are responsible for the characteristic electronic shell structure of

atoms. In DFT, however, the two-electron repulsion integrals are bypassed and instead the repulsion potentials are obtained as functional of electron density. Keeping in mind the key features of these two different classes of methods, here we formulate a new methodology using the electron density approach of DFT and the two-electron integrals of *ab-initio* methods with some modification. It is obvious that for every atomic or molecular property there is a definite unique relation with the parameters on which it depends. That relation may not necessarily be simple or straightforward. However, if that exact relation could be established, calculation of that particular property would be trivial and fast. In this work we have made an attempt to find some such relations.

Within the broad domain of Hohenberg-Kohn-Sham [10, 11] DFT, the single-particle electron density uniquely defines the external potential and energy of a many-electron system. In other words, the energy of such a system is a function of electron density only. Thus,

$$E = g\{\rho\} \tag{2.1}$$

The function g is unknown, and $\rho$ is given in terms of the number of electron$(N)$ and volume$(V)$ as

$$\rho = \frac{N}{V} \tag{2.2}$$

Though, it is obvious that in general, the electron density is not uniform for an interacting many-electron system; however, for simplicity, such an approximation may be considered, particularly for an atom. Assuming spherical symmetry, $V$ is proportional to $r^3$, and hence from Eqs. (2.1) and (2.2), energy of an atom may be written in the following general form,

$$E = K_b N^m \rho^n \tag{2.3}$$

where $K_b$ is a proportionality constant; $m$ and $n$ are two unknowns. But, if we calculate density as a function of $r$ only, we should end up with something like the core potential in *ab-initio* methods, though its value may not be the same. Thus, it is necessary to add the effects of two-electron interactions. Since shell free electrons are considered, total number of two-electron interactions $(T)$ for an $N$-electron atom would be $\frac{N(N-1)}{2}$. Thus, for an $N$ electron system, total energy may be rewritten as,

$$E = K_b N^m \rho^n + K_c T^p \tag{2.4}$$

where $K_c$ is another constant and $p$ is a function of $N$. Equation 2.4 is exact in the sense that it takes into account all the relevant contributions to energy.

To evaluate these constants Hydrogen atom is chosen as a reference. In order to launch the process, an arbitrary guess of $n = 0.1$ is used (other values of $n$ produce similar qualitative results overall, with $n = 0.1$ offering only slightly better values). Using the ground-state energy of $-0.5$ a.u., radius 0.52977$\mathring{A}$ and $N = 1$, $K_b$ is found to be $-$0.4767, from Eq. (3). To evaluate $m$ and $K_c$, two-electron atoms with $T = 1$ is chosen, for which the energy expression may be given as,

$$E = -0.4767 \times 2^m \rho^{0.1} + K_c \tag{2.5}$$

Now four two-electron atoms are chosen, namely $He, Li^+, Be^{2+}, B^{3+}$. Using their ground-state energies as $-2.9070, -7.2930, -13.9996$ and $-23.26153$ a.u. respectively [9], and keeping $K_c$ fixed, 6 $m$ values can be obtained considering the six paired equations (six pairs of atoms). Obviously $m$ is a Z-dependent function, and here we use the form as $m = Z^{1/Z}$. Employing this $m$ for He, gives a value of $K_c = -1.40024$, which is used henceforth. There is no straightforward way to evaluate $p$. But clearly, it should be a function of Z and N. One way to proceed is to split $K_c$ into two parts to account for the Z- and N-dependence separately. The former is incorporated by adding a term in the energy expression which is a function of $m$ and for the latter, a power term in N is introduced. Taking known energies of atoms $(Z = 3 - 10)$ from ref. [9], parametrized form of our energy expression obtained by minimizing the per cent deviation for these atoms keeping the splitting of $K_c$ as $-1.1$ and $-0.30024$ fixed. These atoms are chosen for parametrization because it is known that electron correlation effects are more significant for lower-Z atoms. With this parametrization scheme, one finally gets an expression of energy as follows,

$$E = -0.4767N^m\rho^{0.1} - 1.1T^{(0.2+0.489m+\frac{0.525}{m})} - 0.30024T^{(0.01N^{0.984})} \quad (2.6)$$

Now we move on to the ionization energy. As there is no shell structure and no orbital picture in this approach, ionization energy cannot be obtained directly as the energy difference between $(N-1)$- and $N$-electron systems, which actually reflects the orbital energy of the $N^{th}$ electron according to Koopmans' theorem. However, it is possible to get an approximate expression for ionization energy by using the above idea slightly differently. One can evaluate different orbital energies as an one-electron functions using an *effective radius* and exact nuclear charge. Then the effects of other electrons should reflect through the raise of the power of density operator. Thus, $i^{th}$ orbital energy may be calculated through the expression given below,

$$E_i = [-0.4767\rho^{(n+q)}]_{r=S\times r_0} \quad (2.7)$$

Density $\rho$ in equation 2.7 should be calculated with an effective radius ($r$) which is $S$ times the equilibrium radius ($r_0$). The actual values of $q$ and $S$ depend on which orbital energy one is looking for. The values of $q$ and $S$ are estimated from a consideration of the experimental ionization energies of He, Li and Ne. Using these ionization energy values and known equilibrium radii ($r_0$), Eq. (7) is written for 3 pair of atoms to fix $n$. For each such pair, three different $q$ and $S$ are obtained; taking a mean gives these values as 0.206 and 0.64. This leads to the following simple expression for the $1^{st}$ ionization energy of a given atom,

$$IP = [-0.4767\rho^{0.306}]_{r=0.64r_0}. \quad (2.8)$$

Equations 2.6 and 2.8 are used for energy and ionization energy of atoms. It is envisaged that, for each such property of the system under consideration, there is an exact expression in terms of the parameters. By establishing such an exact relation for such a property of interest, various parameters are obtained by fixing an appropriate one initially and then the others subsequently from it in a stepwise fashion. As such, development of such relations, remains the main objective here. This work presents such relations for ground-state energy and ionization energy of an arbitrary atom in terms of its radius, atomic number and the number of electrons, following some simple arguments. Note that, using Eq. (2.8) one could possibly calculate atomic radii from reference experimental ionization [12] energy as well; however in a reverse way. Finally, other properties such as electron affinity could also be considered in a similar manner.

# 3 RESULTS AND DISCUSSION

At first, the total ground-state energies and $1^{st}$ ionization energies of atoms calculated using the methodology presented above, are presented. For all the atoms up to $Z = 96$, the experimental radii are taken from Dalton Transaction vol. 21, pp-2832 (2008) [13]. For higher Z, these are not available and an approximate radii of $1.40\mathring{A}$ has been used. This could be partly justified considering the fact that for heavier atoms density contribution to the total energy is quite small (less than $0.001\%$ for $Z = 96$). Table **??** gives a comparison of our energies (in a.u.) with relativistic (RHF) and non-relativistic Hartree Fock (NHF) results [9]. Both positive and negative deviations are found in energy relative to the RHF; present energies are lower and higher than the reference values in 70 and 48 occasions. This could happen as the method is not subject to the variational bound. The absolute per cent deviations with respect to RHF and NHF values are given in columns 6,7 respectively. The mean per cent deviation and mean absolute per cent deviation with respect to RHF are found to be 0.0054 and 0.887 respectively. In the former case, there is obviously cancellation of errors. The absolute per cent deviation remains within the range of 0.00–1.40% (Lr, Rf), excepting the cases of Li(11.76%), Be(4.37%), C(1.45%), N(2.5%), O(2.58%), F(2.56%) and Ne(2.54%). Our results agree better with RHF than the NHF values (see percent absolute deviation in Table 1). The absolute deviation with respect to NHF goes as high as 20.36% (ubq), and the mean absolute per cent error reaching 5.72. The deviation in NHF generally shows a trend of

gradual increase leaving aside a few exceptions as seen from column 7. From He to Li, the absolute deviation suddenly jumps to the maximum ($11.77\%$) which could be partly due to the large increase in radius from 0.49 to 2.05 a.u. As one moves through Li to Be to B, the agreement in energy with the reference tends to be better due to a gradual decrease in radius with increase of Z. Within the $2s^2 2p^n$ configuration, maximum deviation is observed for O ($2.58\%$) which may be due to an electronic configuration which breaks a half-filled symmetry. Also it is seen that, after every $p^6$ electronic configuration there is a change of trend in the sense that the absolute difference reaches a maximum in a $p^6$ configuration; then starts to increase with increase in Z, finally reaching a maximum again in the next $p^6$ configuration. For the third row atoms Na, Mg, Al, Si, present method recovers almost 99% of the total energy. After Ca, the per cent errors in column 7 continuously increases always remaining higher compared to those in column 6, presumably because of the relativistic effects becoming progressively more important.

Next, the ionization energies of atoms for $Z = 2 - 96$ are reported in columns 8,9. These are compared with the experimental results [14] and the overall agreement appears to be good. In this case also, both positive and negative variations are observed. Mean absolute deviation is $0.023$ a.u., whereas the mean absolute per cent deviation is $8.73$. As there is a different independent relation for different property in this approach, agreement or disagreement for a particular property is not reflected in other properly, which could probably be quite advantageous in some occasions. Error in energy calculation for a given atom has no bearing on its ionization energy; for example, energy of Be shows a deviation of $4.38\%$ but its ionization energy is very good with respect to the experimental value ($0.6\%$). Deviation is generally found to be more in those cases where ionization leads to a half-filled or completely filled $s$, $p$ or $d$ orbital.

**Table 1. Calculated energies and ionization energies using the present approach and comparison with NHF and RHF results. All quantities in a.u. PW=Present Work. AD=Absolute Deviation. PAD=Per cent Absolute Deviation. See text for details.**

| Atom | Radius | −Energy (a.u.) | | | PAD | | IE (a.u.) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ($\AA$) | PW | NHF [9] | RHF [9] | RHF | NHF | PW | Expt.[14] | AD | PAD |
| H | 0.529 | 0.50001 | 0.50000 | 0.50001 | 0.00 | 0.00 | | | | |
| He | 0.49 | 2.86175 | 2.86168 | 2.86175 | 0.00 | 0.00 | 0.8917 | 0.9026 | 0.0109 | $-1.21$ |
| Li | 2.05 | 6.55891 | 7.43273 | 7.43327 | 11.76 | 11.76 | 0.2397 | 0.1979 | 0.0417 | $21.08$ |
| Be | 1.40 | 13.9377 | 14.5730 | 14.5752 | 4.37 | 4.36 | 0.3401 | 0.3422 | 0.0021 | $-0.60$ |
| B | 1.27 | 24.2933 | 24.5291 | 24.5350 | 0.99 | 0.96 | 0.3720 | 0.3047 | 0.0673 | $22.08$ |
| C | 1.01 | 38.2184 | 37.6597 | 37.6732 | 1.45 | 1.48 | 0.4590 | 0.4134 | 0.0457 | $11.05$ |
| N | 0.85 | 55.7009 | 54.2962 | 54.3229 | 2.54 | 2.59 | 0.5378 | 0.5336 | 0.0042 | $0.79$ |
| O | 0.80 | 76.7498 | 74.7692 | 74.8172 | 2.58 | 2.65 | 0.5686 | 0.5000 | 0.0686 | $13.71$ |
| F | 0.68 | 102.041 | 99.4094 | 99.4897 | 2.56 | 2.65 | 0.6600 | 0.6395 | 0.0205 | $3.21$ |
| Ne | 0.58 | 131.555 | 128.547 | 128.674 | 2.24 | 2.34 | 0.7638 | 0.7916 | 0.0278 | $-3.51$ |
| Na | 2.23 | 160.838 | 161.858 | 162.052 | 0.75 | 0.63 | 0.2219 | 0.1887 | 0.0332 | $17.57$ |
| Mg | 1.72 | 199.007 | 199.615 | 199.901 | 0.45 | 0.30 | 0.2816 | 0.2808 | 0.0007 | $0.26$ |
| Al | 1.82 | 240.984 | 241.877 | 242.286 | 0.54 | 0.37 | 0.2673 | 0.2198 | 0.0476 | $21.66$ |
| Si | 1.46 | 288.669 | 288.834 | 289.403 | 0.25 | 0.06 | 0.3273 | 0.2992 | 0.0281 | $9.39$ |
| P | 1.23 | 341.273 | 340.648 | 341.420 | 0.04 | 0.18 | 0.3831 | 0.3851 | 0.0020 | $-0.53$ |
| S | 1.09 | 398.883 | 397.479 | 398.502 | 0.10 | 0.35 | 0.4280 | 0.3803 | 0.0477 | $12.54$ |
| Cl | 0.97 | 461.807 | 459.481 | 460.821 | 0.21 | 0.51 | 0.4764 | 0.4761 | 0.0002 | $0.05$ |
| Ar | 0.88 | 530.104 | 526.817 | 528.539 | 0.30 | 0.62 | 0.5209 | 0.5786 | 0.0576 | $-9.96$ |
| K | 2.37 | 598.856 | 599.164 | 601.351 | 0.42 | 0.05 | 0.2098 | 0.1594 | 0.0504 | $31.65$ |
| Ca | 2.23 | 677.917 | 676.758 | 679.502 | 0.23 | 0.17 | 0.2219 | 0.2244 | 0.0026 | $-1.14$ |
| Sc | 2.09 | 762.817 | 759.736 | 763.133 | 0.04 | 0.41 | 0.2355 | 0.2401 | 0.0046 | $-1.93$ |

Table 1: (continued)

| Atom | Radius | −Energy (a.u.) | | | PAD | | IE (a.u.) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ($\mathring{A}$) | PW | NHF[9] | RHF[9] | RHF | NHF | PW | Expt.[14] | AD | PAD |
| Ti | 2.00 | 853.567 | 848.370 | 852.531 | 0.12 | 0.61 | 0.2452 | 0.2504 | 0.0052 | $-2.08$ |
| V | 1.92 | 950.362 | 942.804 | 947.851 | 0.26 | 0.80 | 0.2545 | 0.2474 | 0.0071 | $2.87$ |
| Cr | 1.85 | 1053.31 | 1043.14 | 1049.20 | 0.39 | 0.98 | 0.2634 | 0.2485 | 0.0148 | $5.97$ |
| Mn | 1.79 | 1162.53 | 1149.63 | 1156.87 | 0.49 | 1.12 | 0.2715 | 0.2729 | 0.0015 | $-0.55$ |
| Fe | 1.72 | 1278.20 | 1262.29 | 1270.88 | 0.58 | 1.26 | 0.2816 | 0.2889 | 0.0073 | $-2.54$ |
| Co | 1.67 | 1400.33 | 1381.31 | 1391.42 | 0.64 | 1.38 | 0.2893 | 0.2885 | 0.0008 | $0.26$ |
| Ni | 1.62 | 1529.08 | 1506.81 | 1518.64 | 0.69 | 1.48 | 0.2975 | 0.2803 | 0.0172 | $6.14$ |
| Cu | 1.57 | 1664.58 | 1638.95 | 1652.70 | 0.72 | 1.56 | 0.3062 | 0.2836 | 0.0226 | $7.95$ |
| Zn | 1.53 | 1806.87 | 1777.84 | 1793.78 | 0.73 | 1.63 | 0.3135 | 0.3449 | 0.0313 | $-9.09$ |
| Ga | 1.81 | 1954.74 | 1923.26 | 1941.63 | 0.68 | 1.64 | 0.2687 | 0.2202 | 0.0485 | $22.01$ |
| Ge | 1.52 | 2112.03 | 2075.34 | 2096.41 | 0.74 | 1.77 | 0.3154 | 0.2900 | 0.0254 | $8.77$ |
| As | 1.33 | 2276.26 | 2234.16 | 2258.28 | 0.80 | 1.88 | 0.3565 | 0.3601 | 0.0036 | $-1.00$ |
| Se | 1.22 | 2447.41 | 2399.84 | 2427.30 | 0.83 | 1.98 | 0.3860 | 0.3580 | 0.0280 | $7.81$ |
| Br | 1.12 | 2625.94 | 2572.43 | 2603.59 | 0.86 | 2.08 | 0.4175 | 0.4336 | 0.0161 | $-3.71$ |
| Kr | 1.03 | 2811.92 | 2752.06 | 2787.28 | 0.88 | 2.18 | 0.4508 | 0.5140 | 0.0631 | $-12.28$ |
| Rb | 2.98 | 2996.08 | 2938.36 | 2978.07 | 0.61 | 1.96 | 0.1700 | 0.1535 | 0.0166 | $10.79$ |
| Sr | 2.25 | 3198.28 | 3131.55 | 3176.17 | 0.70 | 2.13 | 0.2200 | 0.2091 | 0.0110 | $5.25$ |
| Y | 2.27 | 3406.09 | 3331.67 | 3381.67 | 0.72 | 2.23 | 0.2183 | 0.2342 | 0.0160 | $-6.81$ |
| Zr | 2.16 | 3622.15 | 3538.96 | 3594.81 | 0.76 | 2.35 | 0.2284 | 0.2511 | 0.0227 | $-9.02$ |
| Nb | 2.08 | 3846.01 | 3753.48 | 3815.66 | 0.79 | 2.46 | 0.2365 | 0.2526 | 0.0161 | $-6.36$ |
| Mo | 2.01 | 4077.79 | 3975.37 | 4044.44 | 0.82 | 2.58 | 0.2441 | 0.2606 | 0.0166 | $-6.37$ |
| Tc | 1.95 | 4317.61 | 4204.60 | 4281.18 | 0.85 | 2.69 | 0.2509 | 0.2673 | 0.0163 | $-6.11$ |
| Ru | 1.89 | 4565.59 | 4441.45 | 4526.10 | 0.87 | 2.79 | 0.2582 | 0.2706 | 0.0123 | $-4.55$ |
| Rh | 1.83 | 4821.80 | 4685.83 | 4779.22 | 0.89 | 2.90 | 0.2660 | 0.2739 | 0.0079 | $-2.87$ |
| Fd | 1.79 | 5086.23 | 4937.91 | 5046.70 | 0.78 | 3.00 | 0.2715 | 0.3062 | 0.0347 | $-11.34$ |
| Ag | 1.75 | 5359.06 | 5197.70 | 5310.66 | 0.91 | 3.10 | 0.2771 | 0.2781 | 0.0010 | $-0.35$ |
| Cd | 1.71 | 5640.37 | 5465.12 | 5589.04 | 0.92 | 3.21 | 0.2831 | 0.3301 | 0.0471 | $-14.25$ |
| In | 2.00 | 5928.38 | 5740.16 | 5875.83 | 0.89 | 3.28 | 0.2452 | 0.2124 | 0.0328 | $15.42$ |
| Sn | 1.72 | 6228.19 | 6022.91 | 6171.20 | 0.92 | 3.41 | 0.2816 | 0.2696 | 0.0120 | $4.44$ |
| Sb | 1.53 | 6536.46 | 6313.43 | 6475.24 | 0.95 | 3.53 | 0.3135 | 0.3172 | 0.0037 | $-1.15$ |
| Te | 1.42 | 6853.11 | 6611.75 | 6788.06 | 0.96 | 3.65 | 0.3357 | 0.3308 | 0.0050 | $1.51$ |
| I | 1.32 | 7178.67 | 6917.97 | 7109.75 | 0.97 | 3.77 | 0.3590 | 0.3836 | 0.0246 | $-6.41$ |
| Xe | 1.24 | 7513.11 | 7232.14 | 7440.45 | 0.98 | 3.89 | 0.3802 | 0.4453 | 0.0651 | $-14.61$ |
| Cs | 3.34 | 7844.74 | 7553.93 | 7779.91 | 0.83 | 3.85 | 0.1531 | 0.1430 | 0.0102 | $7.11$ |
| Ba | 2.78 | 8198.21 | 7883.54 | 8128.33 | 0.86 | 3.99 | 0.1812 | 0.1913 | 0.0101 | $-5.29$ |
| La | 2.74 | 8559.22 | 8221.07 | 8485.87 | 0.86 | 4.11 | 0.1836 | 0.2048 | 0.0212 | $-10.35$ |
| Ce | 2.70 | 8929.52 | 8566.84 | 8852.82 | 0.87 | 4.23 | 0.1861 | 0.2034 | 0.0172 | $-8.48$ |
| Pr | 2.67 | 9309.15 | 8921.07 | 9229.40 | 0.86 | 4.35 | 0.1881 | 0.2004 | 0.0124 | $-6.18$ |
| Nd | 2.64 | 9698.23 | 9283.70 | 9615.86 | 0.86 | 4.47 | 0.1900 | 0.2030 | 0.0130 | $-6.40$ |
| Pm | 2.62 | 10096.8 | 9654.87 | 10012.2 | 0.84 | 4.58 | 0.1913 | 0.2039 | 0.0125 | $-6.15$ |
| Sm | 2.59 | 10505.0 | 10034.5 | 10418.7 | 0.83 | 4.69 | 0.1934 | 0.2070 | 0.0137 | $-6.60$ |
| Eu | 2.56 | 10922.9 | 10423.0 | 10835.5 | 0.81 | 4.80 | 0.1955 | 0.2081 | 0.0127 | $-6.10$ |
| Gd | 2.54 | 11350.6 | 10820.0 | 11262.5 | 0.78 | 4.90 | 0.1969 | 0.2258 | 0.0289 | $-12.80$ |
| Tb | 2.51 | 11788.2 | 11226.2 | 11700.2 | 0.75 | 5.01 | 0.1990 | 0.2151 | 0.0161 | $-7.48$ |
| Dy | 2.49 | 12235.7 | 11641.2 | 12148.7 | 0.72 | 5.11 | 0.2005 | 0.2181 | 0.0176 | $-8.06$ |
| Ho | 2.47 | 12693.2 | 12065.0 | 12607.7 | 0.68 | 5.21 | 0.2020 | 0.2210 | 0.0190 | $-8.60$ |
| Er | 2.45 | 13160.9 | 12498.0 | 13078.0 | 0.63 | 5.30 | 0.2035 | 0.2239 | 0.0204 | $-9.13$ |

Table 1: (continued)

| Atom | Radius | −Energy (a.u.) | | | PAD | | IE (a.u.) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | ($\mathring{A}$) | PW | NHF[9] | RHF[9] | RHF | NHF | PW | Expt.[14] | AD | PAD |
| Tm | 2.42 | 13638.9 | 12940.2 | 13559.2 | 0.59 | 5.40 | 0.2058 | 0.2270 | 0.0212 | −9.34 |
| Yb | 2.40 | 14127.2 | 13391.5 | 14051.9 | 0.54 | 5.49 | 0.2074 | 0.2296 | 0.0222 | −9.67 |
| Lu | 2.25 | 14626.6 | 13851.7 | 14555.9 | 0.49 | 5.59 | 0.2200 | 0.1992 | 0.0209 | 10.47 |
| Hf | 2.16 | 15136.3 | 14321.2 | 15071.2 | 0.43 | 5.69 | 0.2284 | 0.2441 | 0.0157 | −6.42 |
| Ta | 2.09 | 15656.6 | 14799.7 | 15598.2 | 0.37 | 5.79 | 0.2355 | 0.2896 | 0.0542 | −18.71 |
| W | 2.02 | 16187.6 | 15287.4 | 16136.9 | 0.31 | 5.89 | 0.2429 | 0.2930 | 0.0500 | −17.07 |
| Re | 1.51 | 16733.6 | 15784.4 | 16687.4 | 0.28 | 6.01 | 0.3173 | 0.2893 | 0.0281 | 9.70 |
| OS | 1.44 | 17286.9 | 16290.5 | 17249.9 | 0.21 | 6.12 | 0.3315 | 0.3194 | 0.0121 | 3.78 |
| Ir | 1.41 | 17850.8 | 16806.0 | 17824.5 | 0.15 | 6.22 | 0.3379 | 0.3341 | 0.0039 | 1.16 |
| Pt | 1.36 | 18426.3 | 17331.0 | 18411.6 | 0.08 | 6.32 | 0.3493 | 0.3304 | 0.0189 | 5.73 |
| Au | 1.36 | 19012.5 | 17865.4 | 19011.3 | 0.01 | 6.42 | 0.3493 | 0.3387 | 0.0107 | 3.15 |
| Hg | 1.32 | 19610.9 | 18409.0 | 19623.5 | 0.06 | 6.53 | 0.3590 | 0.3833 | 0.0242 | −6.32 |
| Tl | 2.08 | 20212.6 | 18961.8 | 20248.3 | 0.18 | 6.60 | 0.2365 | 0.2242 | 0.0123 | 5.47 |
| Pb | 1.81 | 20836.1 | 19524.0 | 20886.0 | 0.24 | 6.72 | 0.2687 | 0.2722 | 0.0035 | −1.30 |
| Bi | 1.63 | 21471.2 | 20095.5 | 21536.6 | 0.30 | 6.85 | 0.2958 | 0.2680 | 0.0278 | 10.38 |
| Po | 1.53 | 22118.0 | 20676.5 | 22200.6 | 0.37 | 6.97 | 0.3135 | 0.3091 | 0.0044 | 1.43 |
| At | 1.43 | 22777.2 | 21266.9 | 22878.1 | 0.44 | 7.10 | 0.3336 | 0.3543 | 0.0207 | −5.83 |
| Rn | 1.34 | 23449.2 | 21866.8 | 23569.0 | 0.51 | 7.24 | 0.3541 | 0.3946 | 0.0405 | −10.27 |
| Fr | 2.60 | 24121.0 | 22475.9 | 24237.8 | 0.48 | 7.32 | 0.1927 | 0.1406 | 0.0521 | 37.05 |
| Ra | 2.21 | 24820.3 | 23094.3 | 24992.3 | 0.69 | 7.47 | 0.2237 | 0.1938 | 0.0299 | 15.41 |
| Ao | 2.15 | 25530.9 | 23722.1 | 25724.9 | 0.75 | 7.62 | 0.2294 | 0.1898 | 0.0396 | 20.88 |
| Th | 2.06 | 26255.4 | 24359.5 | 26471.9 | 0.82 | 7.78 | 0.2386 | 0.2232 | 0.0154 | 6.90 |
| Pa | 2.00 | 26993.8 | 25007.0 | 27233.6 | 0.88 | 7.94 | 0.2452 | 0.2162 | 0.0289 | 13.39 |
| U | 1.96 | 27746.3 | 25664.1 | 28010.5 | 0.94 | 8.11 | 0.2498 | 0.2221 | 0.0277 | 12.45 |
| Np | 1.90 | 28513.9 | 26331.3 | 28802.9 | 1.00 | 8.29 | 0.2570 | 0.2272 | 0.0298 | 13.09 |
| Pu | 1.87 | 29296.4 | 27008.5 | 29610.8 | 1.06 | 8.47 | 0.2608 | 0.2225 | 0.0383 | 17.22 |
| Am | 1.80 | 30094.9 | 27695.5 | 30434.9 | 1.12 | 8.66 | 0.2701 | 0.2199 | 0.0502 | 22.82 |
| Cm | 1.69 | 30910.1 | 28392.4 | 31275.0 | 1.17 | 8.87 | 0.2862 | 0.2210 | 0.0652 | 29.49 |
| Bk | 1.40 | 31744.6 | 29099.9 | 32132.0 | 1.21 | 9.09 | | | | |
| Cf | 1.40 | 32592.6 | 29817.3 | 33006.1 | 1.25 | 9.31 | | | | |
| Es | 1.40 | 33458.4 | 30544.9 | 33897.1 | 1.29 | 9.54 | | | | |
| Fm | 1.40 | 34342.8 | 31282.6 | 34806.3 | 1.33 | 9.78 | | | | |
| Md | 1.40 | 35246.6 | 32030.9 | 35733.1 | 1.36 | 10.04 | | | | |
| No | 1.40 | 36170.7 | 32789.5 | 36679.1 | 1.39 | 10.31 | | | | |
| Lr | 1.40 | 37116.0 | 33558.1 | 37643.1 | 1.40 | 10.60 | | | | |
| Rf | 1.40 | 38083.5 | 34336.6 | 38624.5 | 1.40 | 10.91 | | | | |
| Db | 1.40 | 39074.4 | 35125.5 | 39627.1 | 1.39 | 11.24 | | | | |
| Sg | 1.40 | 40089.9 | 35924.6 | 40649.5 | 1.38 | 11.59 | | | | |
| Bh | 1.40 | 41131.5 | 36734.1 | 41692.5 | 1.35 | 11.97 | | | | |
| Hs | 1.40 | 42200.6 | 37554.1 | 42756.6 | 1.30 | 12.37 | | | | |
| Mt | 1.40 | 43298.9 | 38384.3 | 43642.3 | 0.79 | 12.80 | | | | |
| Ds | 1.40 | 44428.4 | 39225.1 | 44950.1 | 1.16 | 13.27 | | | | |
| Rg | 1.40 | 45591.1 | 40076.1 | 46080.3 | 1.06 | 13.76 | | | | |
| Cn | 1.40 | 46789.2 | 40937.8 | 47234.1 | 0.94 | 14.29 | | | | |
| uut | 1.40 | 48025.3 | 41809.5 | 48411.6 | 0.80 | 14.87 | | | | |
| uuq | 1.40 | 49302.1 | 42691.6 | 49613.6 | 0.63 | 15.48 | | | | |
| uup | 1.40 | 50622.8 | 43584.1 | 50841.1 | 0.43 | 16.15 | | | | |

Table 1: (continued)

| Atom | Radius | −Energy (a.u.) | | | PAD | | IE (a.u.) | | |
|---|---|---|---|---|---|---|---|---|---|
| | ($\mathring{A}$) | PW | NHF[9] | RHF[9] | RHF | NHF | PW Expt.[14] | AD | PAD |
| uuh | 1.40 | 51990.7 | 44487.1 | 52094.6 | 0.20 | 16.87 | | | |
| uus | 1.40 | 53409.6 | 45400.5 | 53375.1 | 0.06 | 17.64 | | | |
| uuo | 1.40 | 54883.7 | 46324.3 | 54683.5 | 0.37 | 18.48 | | | |
| uun | 1.40 | 56417.6 | 47258.5 | 56020.3 | 0.71 | 19.38 | | | |
| ubn | 1.40 | 58016.4 | 48202.8 | 57386.8 | 1.10 | 20.36 | | | |

# 4 CONCLUSION

A simple methodology has been presented for ground-state calculation of atoms. Initial exploratory results for energy and ionization energies have been reported, which compare reasonably well with experimental and theoretical results available in the literature. Working equations containing a few parameters are given for atomic properties following simple arguments. There is no basis dependence and no self consistency as well. There is no real need for computational facilities, storage and computational time. The method could be quite useful for larger systems as there is no computational restriction and as the accuracy is also quite good. Finding the exact relation for a given property is not a straightforward task, and requires caution. For excited state properties, ground state relations may not hold good. But, one could construct valid expressions for different properties in the excited states as well. Implementation of the method for molecular systems would be quite beneficial and may lead to an easy practical route towards the larger systems. Some of these may be taken up in future communications.

## ACKNOWLEDGEMENT

I thank Dr. Amlan Kusum Roy, Associate Professor, IISER Kolkata for his academic help and Dr. Pradip Kr. Ghorai for allow me to publish this work independently.

# COMPETING INTERESTS

Author has declared that no competing interests exist.

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