Near-Exact Non-relativistic Energies for Many-Electron Atoms

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Electron-electron interactions and correlations form the basis of difficulties encountered in the theoretical solution of problems dealing with multi-electron systems. Accurate treatment of the electron-electron problem is likely to unravel some nice physical properties of matter embedded in the interaction. In an effort to tackle this many-body problem, an "exact" form of a symmetry-dependent pseudopotential for an n-electron atom is suggested in this study. The non-relativistic groundstate ionization potentials for atoms with up to 103 electrons generated using this pseudopotential are in good agreement with the existing experimental data. The symmetry dependence in the proposed pseudopotential hinges on a unique partition function specific to a system. An empirically determined partition function used to generate results for the atoms in this study is also presented. We have also calculated explicitly the exchange correlation energy and predicted cases where it is negative, zero, and positive for the various groundstate energy configurations of atoms. The major limitation in the suggested method is its inability to incorporate spin polarization effects which is likely to enhance agreement with experimental results as already observed in DFT calculations.

I. INTRODUCTION

The theory of quantum many-body systems is an effective theoretical structure and solvable approach of understanding the collective behaviour of the interacting many-particle systems[1]. The solution of the many-electron problem is important because electrons determine the physical properties of materials and molecules. Many-body physics is heavily applicable in condensed matter, Bose-Einstein Condensation (BEC) and superfluidity, quantum chemistry, atomic, molecular, nuclear physics, as well as quantum chromodynamics.

Electron correlation energy, among the interacting many-body particles, is defined as the difference between the exact non-relativistic energy eigenvalue of the electronic Schrödinger equation and the energy of the single configuration state function (CSF) approximation, commonly called the Hartree-Fock energy [2].

Accurate description of electron-electron interaction remains a major challenge in atomic structure calculations [2]. To meet this challenge, a number of different methods have been developed such as the many-body perturbation theory (MBPT) [3], configuration interaction (CI)[4], density functional theory [5], coupled cluster theories, and different kinds of variational methods [6]. Hylleraas-type calculations [7] is an example of the variational methods in which the interelectronic distance r_{12} is employed explicitly in the construction of the wavefunction resulting into the most accurate eigenvalues, although computationally expensive.

A pseudopotential is an effective potential used as an approximation for the simplified description of complex atoms, molecules, and other quantum systems. The use of pseudoptentials was first introduced by Fermi [8]. Hellmann [9] subsequently developed a pseudopotential model for atoms which has been extensively used in atomic scattering [10]. The use of pseudopotential method in the many-body problems is computationally less expensive and has the potential of revealing the underlying processes in the interaction dynamics.

In this work, a central screening potential in an independent particle model introduced in our previous papers [11–15], is extended to incorporate the expected symmetry dependence of the electron-electron interaction in the Hamiltonian of an $n-$electron atom. The generalised parameter-free pseudopotential developed in this work is then used to evaluate the groundstate ionization potentials of atoms with up to 103 electrons.

Atomic systems have been chosen to test the validity and efficiency of the present method in predicting experimental data. The atomic systems are not only useful as a playground to for testing physical approximations and numerical algorithms but also provide a basis for understanding complex systems like molecules and condensed matter. Several theoretical studies have been undertaken on atomic systems[16–19] with DFT methods widely adopted. Eventhough DFT method with LSDA and GGA functions have been used to generate total and ionization energies which are in good agreement with experimental results for up to 86 electrons [17, 18], further improvement in the description of atomic systems focussing on non-spherical calculations and on advanced non-local correlation functional is recommended [17].

The symmetry-dependent pseudopotential adopted in this study naturally includes non-spherical terms of the multipole series expansion of the electron-electron interaction. In the present method, we achieve total separability of the Hamiltonian of the many-electron atom and hence the calculations can be considered to yield near-exact non-relativistic eigenvalues. Our results are compared with reported literature data and our previous results [14] based on the classical partitioning of the electron-electron interaction.

II. THEORY

The non-relativistic Hamiltonian of an n-electron system with a nuclear charge Z is given by

$$\mathrm{H} = \sum_{i}^{n} \left[\frac{p_i^2}{2} - \frac{Z}{r_i} + \sum_{j \neq i}^{n-1} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \tag{1}$$

where the first term on the right corresponds to the kinetic energy of the $i^{\mathrm{th}}-$electron, the second term corresponds to the interaction of the $i^{\mathrm{th}}-$electron with the nuclear charge, and the last term in the summation corresponds to the interaction between the $i^{\mathrm{th}}-$ and $j^{\mathrm{th}}-$ electron. The second and the last term form the potential energy function of a bound n-electron system.

In our previous work [11, 20], it was shown that the electron correlation interaction analytically simplifies to

$$\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = \frac{1}{\sqrt{r_i^2 + r_j^2}} \tag{2}$$

within the lowest-order alternative multipole expansion. In the independent particle approximation method, the potential function is given by

$$V(r_i, r_j) = -\frac{Z}{r_i} + \sum_{j \neq i}^{n-1} \gamma_{l_i} \frac{1}{\sqrt{r_i^2 + r_j^2}} \tag{3}$$

for the $i^{\mathrm{th}}-$electron of the system. The coefficient γ_{l_i} defines the ratio for partioning the correlation energy. Conventionally, factor $1/2$ which assumes equal sharing of the correlation energy between the interacting electrons is usually preferred. The interaction potential $V(r_i, r_j)$ can be completely separated, by minimizing it with respect to the spatial co-ordinates, as

$$V(r_i) = -\frac{Z}{r_i} + (n-1)\,\gamma_{l_i} \frac{\left[\frac{Z}{\gamma_{l_i}\,(n-1)}\right]^{1/3}}{r_i} \tag{4}$$

where the spatially-dependent classical partition function

$$\gamma_i(r_i, r_j) = \frac{r_i^2}{r_i^2 + r_j^2}, \tag{5}$$

introduced in ref.[13], is replaced with a corresponding symmetry-dependent partition function which depends, not on the radial coordinates, but on the local orbital angular momentum value (l_i) for the i^{th} state of the system. We employ an empirical and intuitive process of obtaining the symmetry-dependent partition functions used in this study. The pseudoptentials developed in the previous paper [14] and related literature data aid in validating and calibrating the partition function. Indeed, the success of the equal sharing of the electron-electron interaction potential for spherically symmetric cases already hinted to a possibility of such a symmetry-dependent partition function. This hint was successfully used in coming up with a symmetry-dependent partition function for helium atom [12, 15].

The effects of the higher-order electron-electron multipole interactions can be included through the extended potential [15]

$$V(r_i) = -\frac{Z}{r_i} + (n-1)\,\gamma_{l_i} \frac{\left[\frac{Z}{\gamma_{l_i}\,(n-1)}\right]^{1/3}}{r_i} + V_l^{xc}(r_i) \tag{6}$$

where

$$V_l^{xc}(r_i) = (n-1)\,\gamma_{l_i} \frac{\tilde{\beta}_l(Zr_i)}{r_i}\,\delta_{ll_i} \tag{7}$$

with the function

$$\tilde{\beta}_l(Zr_i) = \left[(n-1)\,\gamma_{l_i} \frac{(l+1)}{(l+2)Z}\right]^3 \cos\left[(n-1)\,\gamma_{l_i} \frac{(l+1)}{(l+2)Zr_i}\right] \tag{8}$$

In our working, we established that the symmetry-dependent partition function is sytem specific and largely takes a general form that depends on the symmetry of the valence electrons. For valence electrons with an orbital angular momentum value l_v and an orbital angular momentum l_i for the i^{th} electron, the partition function γ_{l_i} is empirically determined to be

$$\gamma_{l_i} = \frac{1 + \sqrt[\delta_1]{l_i}}{2 + \sqrt[\delta_1]{l_i} + \delta_2} \tag{9}$$

where the root function of l_i is given by

$$\delta_{l_i} = [(n - 0.5) \times (l_i + 0.5)] \tag{10}$$

and a parameter

$$\delta_2 = \frac{l_v}{2^{(2l_v - 1)}} \tag{11}$$

that depends on the valent subshell with l_v being the orbital angular momentum quantum number of the valent electron in the groundstate configuration.

Using the suggested symmetry-dependent pseudopotentials, the one electron Hamiltonian

$$h(r_i) = \frac{p_i^2}{2} + V(r_i) \tag{12}$$

is defined. The eigenvalue ϵ_{α_i} corresponding to state α_i for an n-electron atom can be generalized as

$$\epsilon_{\alpha_i} = \frac{m}{n} \langle \phi_{\alpha_i} | h(\mathbf{r}_i) | \phi_{\alpha_i} \rangle \tag{13}$$

where m refers to the number of non-vanishing integrals out of the $n!$ possible permutations. For lithium, $m/n = 2/3$ as was already shown in our previous paper [14]. In principle, the integer m can be determined from the groundstate configuration of the atom but constrained further by other symmetry considerations. The integer $m-1$ correspond to the number of exchange integrals that contribute to the energy of the system. This shows that apart from helium and alkalis where the exchange integral has an equal weight with the direct integral, in all the other atoms the exchange contribution is greater. Apparently m has a maximum value of 5 for noble gases regardless of the number of electrons present in the atom.

For reference purposes, we have also included results calculated using our previously derived pseudopotential [14]

$$V(r_i) = -\frac{Z}{r_i} + (n-1)\frac{\left[\frac{Z\, f(r_i, r_j)}{2(n-1)}\right]^{3/5}}{r_i} \tag{14}$$

where the expectation value

$$\langle f(r_i, r_j)^{\frac{3}{5}} \rangle \approx 1 - \left[\frac{27}{25} + \frac{3}{5} Z r_i - \frac{6}{125\, Z r_i}\right] \exp(-2 Z r_i) \tag{15}$$

is approximately optimized by evaluating the integral using a trial function for hydrogenic system in the $1s$ state.

III. RESULTS AND DISCUSSIONS

We have developed a symmetry-dependent pseudopotential for an n-electron system defined by equations (4) and (6). The pseudopotentials are used to calculate the groundstate ionization potentials for n-electron atoms as shown in tables I and II with $2 \leq n \leq 103$. Our results are compared with the results of the pseudopotential given by equation (14), DFT calculations [17], and experimental reference data [21]. In generating our results, a B-spline radial box of 600 B-splines, maximum radius $r_{\max} = 200$, order $k = 10$, and a non-linear knot sequence is used.

Tables I and II show some numerically calculated non-relativistic ionization energies for n-electron atoms using the present pseudopotentials given by equations (14), (4), and (6) respectively versus the reference theoretical [17] and experimental values [21]. The table also contains the grounstate orbital, the exchange-correlation energy ϵ_{xc} as well as the symmetry fractions (m/n), already introduced in equation (13), that have been determined and used in the present study. These fractions yield information on the number of exchange integrals contributing to the evaluation

n	Atom	State	m/n	V_{cen}	V_{dir}	V_{dxc}	LSDA	GGA	Exp.(eV)	ϵ_{xc}
2	He	1s	2/2	35.21	24.76	24.60	24.29	24.46	24.58	0.16
3	Li	2s	2/3	4.97	5.50	5.47	5.47	5.58	5.39	0.03
4	Be	2s	3/4	8.90	9.40	9.31	9.02	8.99	9.32	0.09
5	B	2p	3/5	8.08	8.43	8.43	8.57	8.48	8.29	0.00
6	C	2p	4/6	12.29	12.42	11.51	11.76	11.67	11.26	0.91
7	N	2p	4/7	13.82	13.65	14.83	14.99	14.91	14.53	-1.18
8	O	2p	4/8	15.37	14.90	13.54	13.89	13.67	13.61	1.36
9	F	2p	4/9	16.92	16.16	17.79	18.05	17.84	17.42	-1.63
10	Ne	2p	6/10	23.11	21.80	21.80	22.17	21.98	21.56	0.00
11	Na	3s	2/11	5.30	5.55	5.44	5.36	5.35	5.13	0.11
12	Mg	3s	3/12	8.58	8.95	8.76	7.60	7.71	7.64	0.19
13	Al	3p	3/13	7.72	7.10	6.28	5.99	5.96	5.98	0.82
14	Si	3p	4/14	10.99	10.05	8.87	8.27	8.27	8.15	1.18
15	P	3p	4/15	11.69	10.63	10.63	10.53	10.55	10.48	0.00
16	S	3p	4/16	12.39	11.20	9.87	10.53	10.23	10.36	1.33
17	Cl	3p	4/17	13.09	11.79	13.24	13.24	13.05	12.96	-1.45
18	Ar	3p	6/18	17.24	15.46	15.46	15.93	15.80	15.75	0.00
19	K	4s	2/19	4.65	4.97	4.85	4.52	4.44	4.34	0.12
20	Ca	4s	3/20	7.31	7.80	7.61	6.20	6.06	6.11	0.19
21	Sc	3d	4/21	11.86	8.48	6.00	6.54	6.37	6.56	2.48
22	Ti	3d	4/22	12.38	8.82	6.23	6.71	6.54	6.82	2.59
23	V	3d	4/23	12.91	9.17	6.47	7.14	6.96	6.74	2.70
24	Cr	3d	4/24	13.43	9.51	6.70	7.45	7.25	6.76	2.81
25	Mn	3d	4/25	13.95	9.86	6.94	7.48	7.15	7.43	2.92
26	Fe	3d	4/26	14.48	10.20	7.18	8.20	7.84	7.90	3.02
27	Co	3d	4/27	15.00	10.55	7.42	8.10	7.89	7.88	3.13
28	Ni	3d	4/28	15.52	10.89	7.67	8.23	8.01	7.63	3.22
29	Cu	3d	4/29	16.05	11.24	7.91	8.38	8.14	7.72	3.33
30	Zn	3d	4/30	16.57	11.58	11.58	9.68	9.37	9.39	0.00
31	Ga	4p	3/31	9.65	8.41	7.40	6.05	5.90	5.99	1.01
32	Ge	4p	4/32	13.27	11.55	10.17	8.06	7.97	7.89	1.41
33	As	4p	4/33	13.66	11.88	10.47	9.97	9.93	9.78	1.41
34	Se	4p	5/34	14.05	12.21	10.77	9.92	9.54	9.75	1.44
35	Br	4p	5/35	14.45	12.54	11.07	12.12	11.87	11.81	1.47
36	Kr	4p	6/36	18.56	16.08	14.22	14.26	14.09	13.99	3.86
37	Rb	5s	2/37	5.42	5.85	5.68	4.32	4.21	4.17	0.17
38	Sr	5s	3/38	8.34	9.01	8.74	5.77	5.61	5.69	0.27
39	Y	4d	3/39	11.97	8.26	5.81	6.24	6.02	6.21	2.45
40	Zr	4d	3/40	12.27	8.46	5.96	6.68	6.48	6.63	2.50
41	Nb	4d	3/41	12.56	8.65	6.11	7.03	6.80	6.75	2.54
42	Mo	4d	3/42	12.86	8.85	6.26	7.29	7.04	7.09	2.59
43	Tc	4d	3/43	13.15	9.04	6.41	7.45	7.21	7.11	2.63
44	Ru	4d	3/44	13.45	9.24	6.57	7.54	7.29	7.36	2.67
45	Rh	4d	3/45	13.74	9.43	6.73	8.29	7.97	7.45	2.70
46	Pd	4d	3/46	14.04	9.63	6.89	9.37	9.08	8.33	2.74
47	Ag	4d	3/47	14.33	9.82	7.05	7.66	7.36	7.57	2.77
48	Cd	4d	3/48	14.63	10.02	10.02	8.85	8.50	8.99	0.00
49	In	5p	3/49	9.58	8.23	7.22	5.77	5.58	5.78	1.01
50	Sn	5p	4/50	13.03	11.18	9.82	7.48	7.36	7.34	1.36
51	Sb	5p	4/51	13.28	11.39	10.01	9.08	9.01	8.60	1.38
52	Te	5p	4/52	13.53	11.60	10.20	9.06	8.69	9.00	1.40
53	I	5p	4/53	13.78	11.82	10.39	10.85	10.59	10.45	1.43
54	Xe	5p	5/54	17.55	15.03	13.22	12.56	12.38	12.12	1.81

TABLE I: Some numerically calculated non-relativistic ionization potentials for $2 \leq n \leq 54$-electron atoms versus the reference values from DFT (LSDA and GGA) calculations [17] and experiment [21]. The Present V_{cent} results are evaluated using equation (14). The present V_{dir} and V_{dxc} are the results evaluated using the symmetry-dependent pseudopotentials given by equations (4) and (6)respectively. The results presented are truncated to 2 d.p.

of the energy eigenvalues. The ionization energies have been obtained using Koopman's theorem [22] except for the grounstate of helium atom which is evaluated as the difference between the total energy of helium atom and the residual

n	Atom	State	m/n	V_{cen}	V_{dir}	V_{dxc}	LSDA	GGA	Exp.(eV)	ϵ_{xc}
55	Cs	6s	2/55	5.42	5.93	5.74	3.94	3.83	3.89	0.19
56	Ba	6s	3/56	8.27	9.05	8.76	5.16	4.97	5.21	0.29
57	La	4f	3/57	17.29	9.87	4.96	5.31	4.98	5.57	4.91
58	Ce	4f	3/58	17.59	10.04	5.05	5.12	4.96	5.53	4.99
59	Pr	4f	3/59	17.88	10.20	5.14	4.99	4.82	5.47	5.06
60	Nd	4f	3/60	18.18	10.36	5.24	4.88	4.70	5.52	5.12
61	Pm	4f	3/61	18.47	10.52	5.33	4.78	4.60	5.58	5.19
62	Sm	4f	3/62	18.77	10.68	5.43	4.70	4.53	5.64	5.25
63	Eu	4f	3/63	19.06	10.85	5.53	5.51	5.33	5.67	5.32
64	Gd	4f	3/64	19.36	11.01	5.63	5.60	5.42	6.14	5.38
65	Tb	4f	3/65	19.65	11.17	5.73	5.49	5.35	5.86	5.44
66	Dy	4f	3/66	19.95	11.33	5.83	5.40	5.26	5.93	5.50
67	Ho	4f	3/67	20.24	11.50	5.94	5.32	5.17	6.02	5.56
68	Er	4f	3/68	20.54	11.66	6.04	5.26	5.10	6.10	5.62
69	Tm	4f	3/69	20.84	11.82	6.15	5.20	5.07	6.18	5.67
70	Yb	4f	3/70	21.13	11.98	6.26	6.00	5.82	6.25	5.72
71	Lu	5d	3/71	13.71	9.28	6.92	6.39	6.18	5.42	2.36
72	Hf	5d	3/72	13.89	9.40	7.03	6.76	6.59	6.82	2.37
73	Ta	5d	3/73	14.08	9.53	7.14	7.23	7.01	7.54	2.39
74	W	5d	3/74	14.27	9.65	7.25	7.49	7.25	7.86	2.40
75	Re	5d	3/75	14.46	9.78	7.36	7.63	7.15	7.83	2.42
76	Os	5d	3/76	14.65	9.90	7.47	7.69	7.45	8.43	2.43
77	Ir	5d	3/77	14.84	10.02	7.58	8.57	8.24	8.96	2.44
78	Pt	5d	3/78	15.03	10.15	7.69	9.67	9.38	8.95	2.46
79	Au	5d	3/79	15.22	10.27	7.80	7.75	7.45	9.22	2.47
80	Hg	5d	3/80	15.41	10.40	10.40	8.82	8.46	10.43	0.00
81	Tl	6p	3/81	10.86	9.23	8.03	5.67	5.46	6.10	1.20
82	Pb	6p	4/82	14.65	12.45	10.83	7.25	7.12	7.41	1.62
83	Bi	6p	4/83	14.83	12.60	10.96	8.71	8.63	7.28	1.64
84	Po	6p	4/84	15.00	12.74	11.08	8.69	8.32	8.41	1.66
85	At	6p	4/85	15.18	12.89	11.21	10.29	10.02	9.31	1.68
86	Rn	6p	5/86	19.19	16.30	14.17	11.81	11.63	10.74	2.13
87	Fr	7s	2/87	6.15	6.78	6.58			4.07	0.20
88	Ra	7s	3/88	9.32	10.29	9.98			5.27	0.31
89	Ac	5f	3/89	17.11	9.64	5.28			5.38	4.36
90	Th	5f	3/90	17.30	9.75	5.37			6.30	4.38
91	Pa	5f	3/91	17.49	9.85	5.46			5.89	4.39
92	U	5f	3/92	17.68	9.95	5.54			6.19	4.41
93	Np	5f	3/93	17.87	10.06	5.63			6.26	4.43
94	Pu	5f	3/94	18.06	10.16	5.72			6.02	4.44
95	Am	5f	3/95	18.25	10.26	5.81			5.97	4.45
96	Cm	5f	3/96	18.44	10.37	5.90			5.99	4.47
97	Bk	5f	3/97	18.62	10.47	6.00			6.19	4.47
98	Cf	5f	3/98	18.81	10.58	6.09			6.28	4.49
99	Es	5f	3/99	19.00	10.68	6.19			6.36	4.49
100	Fm	5f	3/100	19.19	10.78	6.28			6.50	4.50
101	Md	5f	3/101	19.38	10.89	6.38			6.58	4.51
102	No	5f	3/102	19.57	10.99	6.48			6.62	4.51
103	Lr	6d	2/102	13.72	9.21	6.94			4.96	2.27

TABLE II: Same as table I but for $55 \leq n \leq 103$-electron atom.

ion both in their groundstates. The groundstate ionization potentials calculated using the present pseudopotential incorporating the direct and exchange terms (V_{dxc}) as given in equation (6) are in very good agreement with the reference values. The central potential (V_{cen}) given by equation (14) and the direct term (V_{dir}) in equation (6) are both derived from the lowest-order term of the multipole interaction. The results between the two corresponding potentials compare qualitatively but the quantitative difference increase with the atomic nuclear charge (Z). The central potential is derived from the classical partitioning whereas the the symmetry-dependent potential is based on the quantum partitioning of the electron-electron interaction term. The discrepancy between the results generated by the lowest multipole-order based pseudopotentials can be attributed to the approximation involved in the central pseudopotential given by equation (15). Since the calculations involving the symmetry-dependent partition function

can be considered exact, without any approximation used, the results are reliable and are expected to provide the theoretical benchmark within the non-relativistic regime for a correct symmetry-dependent partition function. In deed when the exchange interactions are included into the single-particle Hamiltonian, the results are in close agreement with the experimental results for all the multi-electron atoms. Major discrepancies between the present direct plus exchange potential evaluated results and the experimental results manifest for multi-electron atoms with more than 18 electrons. The discrepancy can be attributed to the dominant role played by the exchange correlation energy, spin polarization effects, and the relativistic effects. It is of desirable interest to include these effects in the future advancement of the suggested method.

The ionization potential for lawrencium ($n = 103$) is experimentally determined to be 4.96 [23] with a groundstate configuration of $[Rn]7s^2 5f^{14} 6d$. This disagrees with the current groundstate calculation of 6.9478 but agrees with our next excited state $[Rn]7s^2 5f^{14} 7d$ calculation of 4.9497 within the limits of experimental error. The correct ionization energy for this state therefore needs to be investigated further.

Figures 1 and 2 graphically represents the results contained in tables I and II. In figure 1, our present results are compared with the experimental results derived from literature. It is evident from the graphs that the exchange correlation energy increases with the nuclear charge as well as orbital angular momentum. It can been seen that the inclusion of the exchange term plays a vital role in accurate determination of the ionization energies of all multi-electron atoms. In figure II, our calculated results incorporating both diect and exchange potentials are compared with DFT calculations with LSDA and GGA exchange correlation functions [17] and with the experimental [21] results. Evidently DFT spin polarised results compare well with experimental results but our calculated results are in close agreement and even better for few-electron atoms ($2 \leq n \leq 10$) and the lanthanide ($57 \leq n \leq 70$) series.

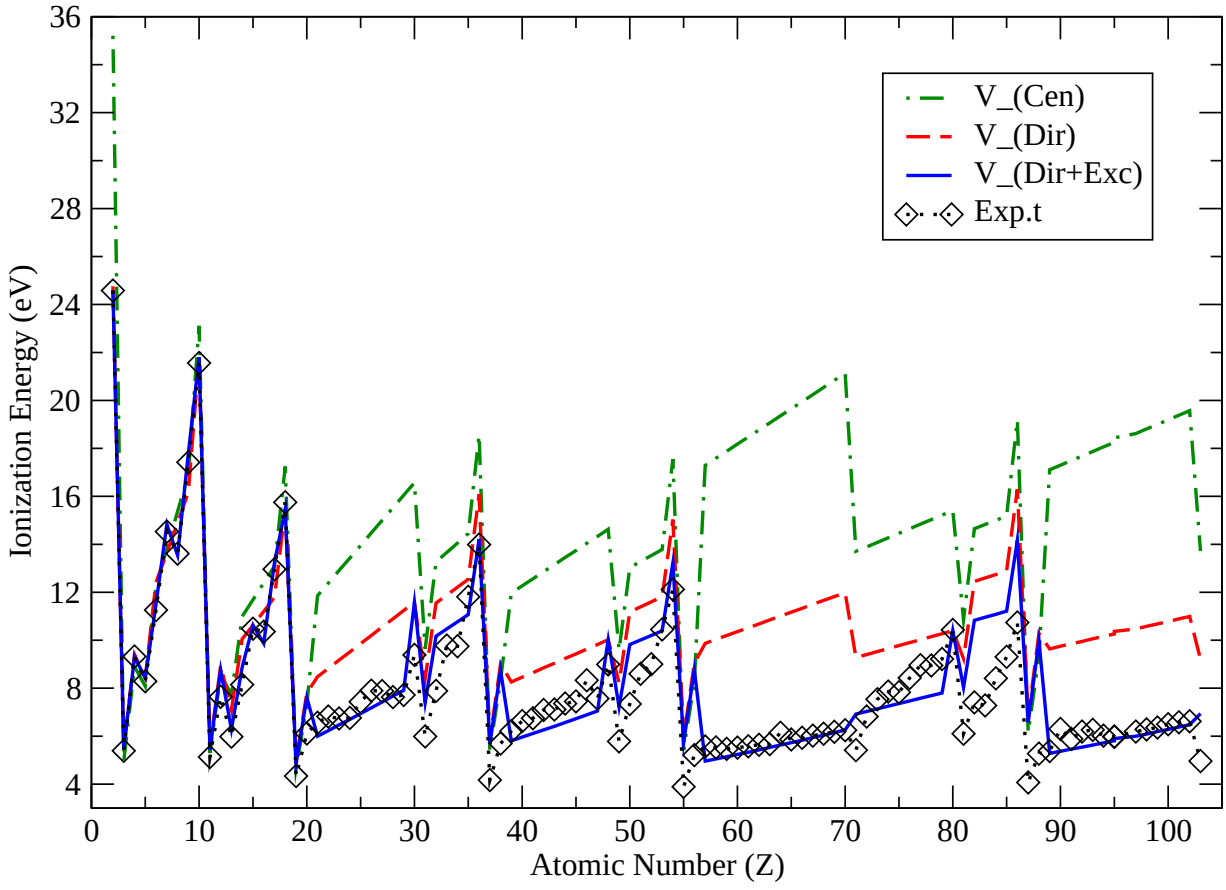

FIG. 1: (Color online) Non-relativistic atomic ionization energies for multi-electron atoms evaluated using various potentials in comparison with experimental results [21].

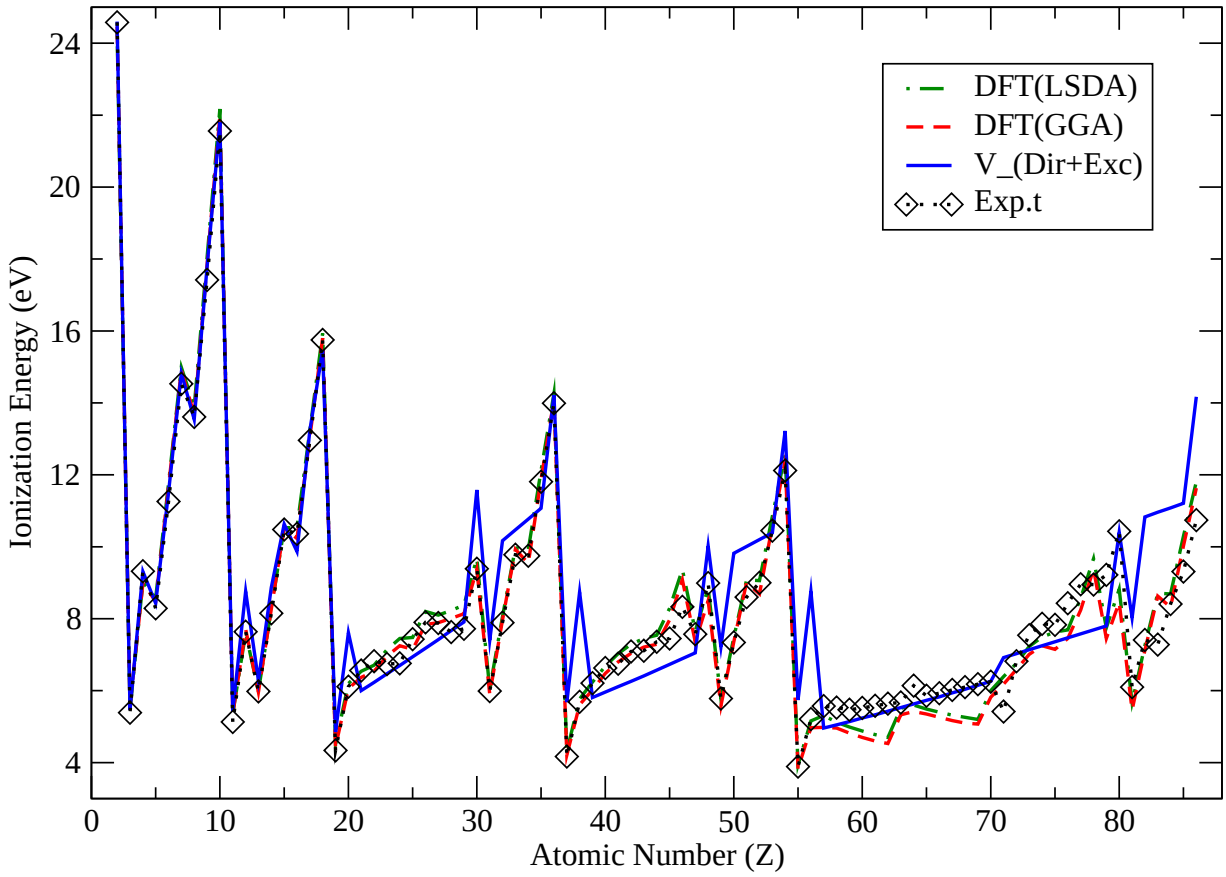

FIG. 2: (Color online) Non-relativistic atomic ionization energies for multi-electron atoms evaluated using our symmetry-dependent direct plus exchange potential in comparison with DFT (LSDA and GGA) [17] and experimental results [21].

Figure 3 shows the exchange correlation energy obtained by subtracting the direct plus exchange interaction ionization results from the direct term only interaction ionization results. This calculation of the exchange correlation energy is different from the expected difference between the exact calculation and the Hartree-Fock limit, which is a maximum. Our calculation is on the other hand relative to the minimum direct potential (V_{dir}) results. We however expect some correspondence between our calculation and the exchange correlation energy relative to the Hartree-Fock limit. The calculated exchange correlation energy is negative where the groundstate of the system corresponds to the triplet state. This is the case for nitrogen, flourine and chlorine atoms. We also have interesting cases where the correlation energy is zero like for boron, neon, phosphorus, argon, zinc, cadmium, and mercury. For these systems, the effect of the exchange potential is ignored because the direct potential (V_{dir}) results gives a better prediction of the experimental results. This implies that for these systems, their is an exact cancellation of the exchange correlation contribution.

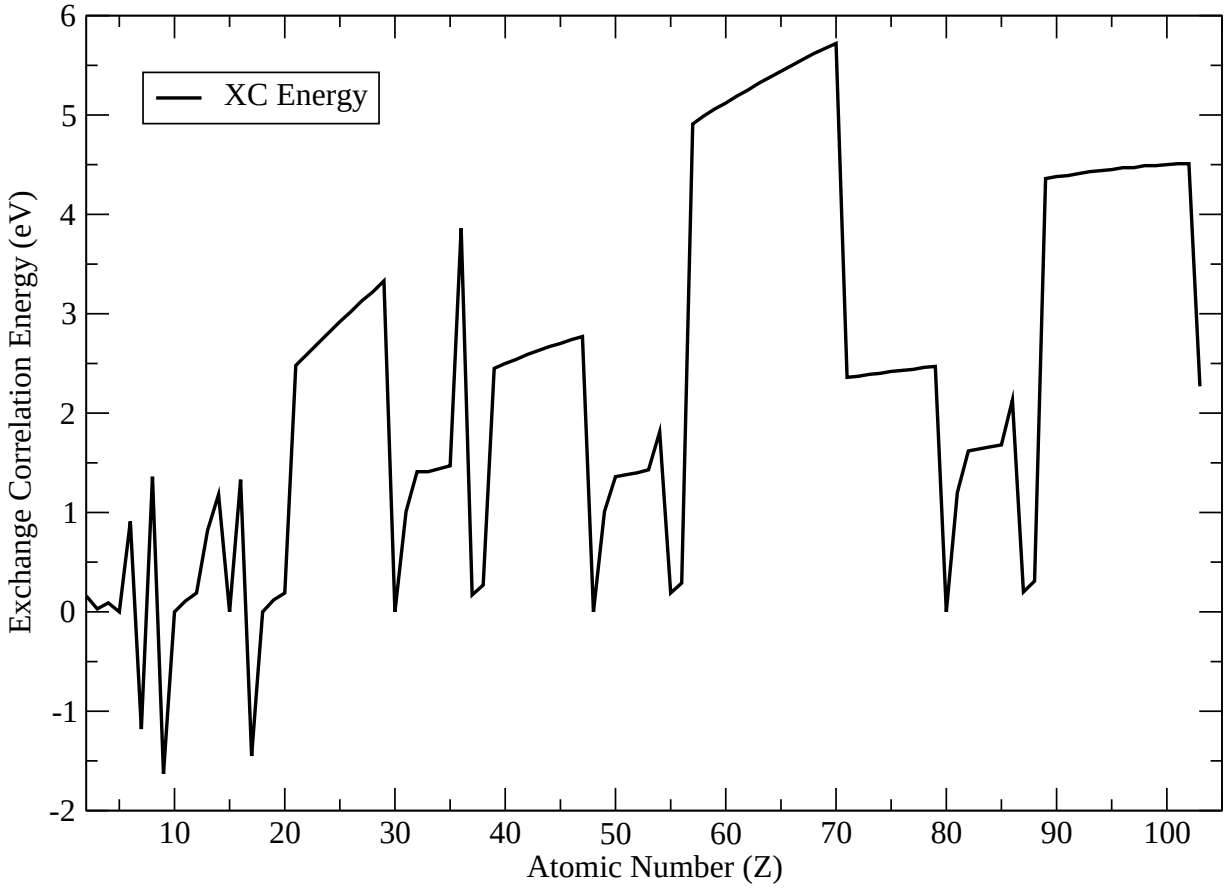

FIG. 3: (Color online) Exchange correlation energies in electronvolts for multi-electron atoms as a function of atomic number.

IV. CONCLUSION

We have derived a symmetry-dependent pseudopotential generalized for n-electron atoms. The performance of the pseudopotential is tested against our previously developed central potential and DFT calculations in reproducing benchmark experimental results. The contribution of the direct and exchange potentials in the various ionization energies is evaluated. The pseudopotential yields reliable groundstate ionization energies relative to literature data. It is also apparent from this work direct integral without exchange can only be used as a first approximation for few-electron ($n \leq 18$) systems. This is indeed the case for our central potential and the lowest-order symmetry dependent potential used in this work. Beyond argon atom, the exchange effects become significant and must be properly accounted for to obtain a better description of the system. The major advantage of the present direct plus exchange pseudopotential is that it leads to a completely separable Hamiltonian for the many-electron atoms. The separability of the Hamiltonian together with the use of the Slater-type determinant expansion of the wavefunction completely describes the system within the non-relativistic quantum mechanics. This is expected to consequently solve electron-electron interaction problem with certainty. The discrepancy between the non-relativistic results generated using the symmetry-dependent pseudopotential and the experimental results available points to the relative importance of the spin-polarization effects, relativistic and other higher-order effects in the interaction dynamics. These higher effects will be investigated further in our subsequent work. From the derived pseudopotential, one can observe that the electron-electron screening is a function of the nuclear charge, orbital angular momentum and radial coordinate of screened electron, and the total number of electrons in the multi-electron system.

V. ACKNOWLEDGEMENT

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