Momentum-space properties of atoms: Application of the generalized-gradient approximation

Rajendra R. Zope*
Department of Physics, University of Pune, Pune 411 007, Maharashtra, India
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The calculations of Compton profiles and various $\langle p^n \rangle$-expectation values are carried out for a few closed-shell atomic systems within Perdew-Burke-Ernzerhof (PBE), Perdew-Wang 1991 (PW91) and Becke-Lee-Yang-Parr (BLYP) generalized-gradient approximations. The calculated Compton profiles and the moments are compared with their local-density approximation (LDA) and more accurate available theoretical or experimental counterparts in order to investigate the supremacy of generalized gradient approximation (GGA) over LDA in predicting the momentum-space properties. The results show that GGA improves the Compton profiles marginally. The PBE and PW91 values of Compton profiles are practically identical and are slightly better than BLYP. Further comparison of GGA and LDA results with those calculated within self-interaction corrected LDA (SICLDA) formalism demonstrates the importance of proper description of the valence region in the study of Compton profiles. GGA values of the moments of electron momentum density are found to be, in general, more accurate than their LDA counterparts.

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Over the last 30 years the density-functional theory, with the local approximation for the exchange-correlation effects has proven to be remarkably successful in predicting various solid-state properties such as lattice constants, bulk moduli, crystal structures, vibrational frequencies, etc. [1–3]. The local-density approximation (LDA) [1,3] is by construction exact for the homogeneous electron gas and therefore is more appropriate for solids than molecules and atoms as these systems are increasingly inhomogeneous. The moderate accuracy achieved using LDA in solids is not sufficient in the study of localized systems such as atoms and molecules. Recently, an improvement over LDA is obtained by means of generalized gradient approximation (GGA) [4–8]. These approximations have made density functional theory a popular and useful tool in quantum chemistry by achieving the accuracy required for the chemical purposes. The calculations of binding energies of solids and molecules using GGA's are more accurate, and to some extent correct the overbinding tendency of LDA [9]. They also improve reaction and activation energies for a variety of chemical reactions [4] and are also found to be more successful than LDA in predicting the relative stability of structural phases for magnetic and nonmagnetic materials [10,11]. Generally, it is observed that in solid-state calculations, GGA corrects binding energies, underestimates bulk moduli [12], and sometimes overcorrects lattice constants [13] compared to local density approximation. Very few studies of momentum-space properties such as Compton profiles of solids have also been reported using GGA [14–16]. The Compton profile studies on bulk lithium using GGA do not show any significant improvement over LDA [14,15] while in silver the anisotropies seem to improve in the low q region. GGA also improves magnetic Compton profiles of Ni [15,16]. Thus, GGA seems to have been partially successful in overcoming

TABLE I. Spherically averaged Compton profile $J_{\mathrm{sph}}(q)$ for helium within the Becke-Lee-Yang-Parr (BLYP), Perdew-Wang (PW91), Perdew-Burke-Ernzerhof (PBE), Ceperley-Alder-Perdew-Zunger (CAPZ) and self-interaction corrected LDA (SICLDA) theories compared with their experimental counterpart. (Hartree atomic units are used throughout.)

q	BLYP	PW91	PBE	CAPZ	SICLDA	Expt. [a]
0.0	1.104	1.103	1.104	1.118	1.052	1.071
0.2	1.043	1.042	1.043	1.055	1.002	1.019
0.4	0.887	0.886	0.887	0.895	0.871	0.705
0.6	0.791	0.791	0.792	0.797	0.700	0.705
0.8	0.514	0.515	0.515	0.515	0.531	0.388
1.0	0.369	0.370	0.370	0.367	0.388	0.388
1.5	0.155	0.156	0.155	0.151	0.164	
2.0	0.067	0.068	0.067	0.064	0.070	0.069
2.5	0.031	0.031	0.031	0.029	0.031	0.030
3.0	0.015	0.015	0.015	0.014	0.015	0.013

[a]Reference [28].

TABLE II. $J_{\mathrm{sph}}(q)$ for neon.

q	BLYP	PW91	PBE	CAPZ	SICLDA	CI [a]	Expt. [b]
0.0	2.785	2.779	2.780	2.787	2.729	2.739	2.762
0.2	2.751	2.745	2.746	2.752	2.696	2.707	2.738
0.4	2.678	2.633	2.634	2.638	2.590	2.602	2.630
0.6	2.436	2.433	2.434	2.438	2.406	2.416	2.427
0.8	2.166	2.165	2.166	2.169	2.159	2.165	2.162
1.0	1.867	1.868	1.870	1.871	1.877	1.880	1.859
1.5	1.198	1.201	1.201	1.199	1.219		
2.0	0.756	0.759	0.758	0.755	0.770	0.768	0.765
2.5	0.498	0.499	0.498	0.497	0.505		0.501
3.0	0.347	0.347	0.347	0.346	0.351	0.348	0.359
3.5	0.255	0.255	0.255	0.255	0.258		0.277
4.0	0.196	0.196	0.195	0.196	0.198	0.196	0.210
5.0	0.126	0.126	0.125	0.126	0.127	0.126	0.126

[a]Reference [30].
[b]Reference [29].

*Present address: Département de Recherche Fondamentale sur Matière Condensée SI2A, CEA Grenoble, 17 rue des Martyrs, F-38054 Grenoble, Cedex 9, France.

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TABLE III. $J_{sph}(q)$ for argon.

q	BLYP	PW91	PBE	CAPZ	SICLDA	Expt. [a]
0.0	5.090	5.077	5.077	5.090	5.045	5.058
0.2	4.988	4.976	4.976	4.988	4.946	4.917
0.4	4.633	4.625	4.626	4.633	4.608	4.526
0.6	4.027	4.026	4.028	4.027	4.027	3.960
0.8	3.309	3.314	3.316	3.310	3.325	3.319
1.0	2.640	2.647	2.648	2.640	2.657	2.697
1.5	1.551	1.556	1.554	1.551	1.552	
2.0	1.091	1.091	1.091	1.091	1.089	1.129
2.5	0.877	0.876	0.876	0.877	0.877	0.904
3.0	0.737	0.736	0.736	0.737	0.738	0.744
3.5	0.620	0.620	0.620	0.620	0.622	0.634
4.0	0.518	0.518	0.518	0.518	0.520	0.534
5.0	0.358	0.358	0.358	0.358	0.359	0.366
10.0	0.076	0.076	0.076	0.076	0.076	0.078
15.0	0.025	0.025	0.025	0.025	0.025	0.025

[a]Reference [28].

TABLE IV. $J_{sph}(q)$ for krypton.

q	BLYP	PW91	PBE	CAPZ	SICLDA	Expt. [a]
0.0	7.250	7.234	7.235	7.233	7.200	7.188
0.2	7.112	7.096	7.098	7.096	7.065	6.988
0.4	6.615	6.606	6.607	6.608	6.591	6.453
0.6	5.779	5.779	5.782	5.785	5.785	5.702
0.8	4.847	4.854	4.856	4.859	4.864	4.883
1.0	4.045	4.054	4.054	4.055	4.057	4.131
2.0	2.452	2.451	2.450	2.453	2.450	2.557
3.0	1.854	1.854	1.854	1.854	1.855	
4.0	1.319	1.319	1.319	1.319	1.321	1.350
5.0	0.931	0.931	0.931	0.930	0.932	0.933
10.0	0.260	0.260	0.260	0.260	0.261	0.254
15.0	0.105	0.105	0.105	0.105	0.105	0.099
20.0	0.050	0.050	0.050	0.050	0.050	
30.0	0.015	0.015	0.015	0.015	0.015	

[a]Reference [28].

the limitations of LDA. However, to the best of our knowledge, the performance of GGA has not yet been tested in the study of momentum-space properties of atoms and also molecules. In this communication, we employ generalized gradient approximation to investigate its effects and in particular, to judge the superiority of GGA over LDA in predicting the momentum-space properties. To this end, we employ the Perdew-Wang (PW91) [5], Becke-Lee-Yang-Parr (BLYP) [6,7], and the recent Perdew-Burke-Ernzerhof (PBE) [8] schemes of GGA to calculate the momentum-space properties such as Compton profile and various moments of momentum density, to compare them against their LDA and experimental and/or more accurate theoretical counterparts whenever available. The PW91 and PBE functionals are constructed in such a manner that they satisfy several exact density-functional properties, like the exchange-correlation sum rule, scaling relations, the Lieb-Oxford bound, etc. For the details we refer the reader to literature [4].

The Compton profile is an experimentally observable quantity through the Compton scattering experiments and is related to the electron momentum density (EMD), through

$$J(q)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\gamma(p_x,p_y,q)dp_x dp_y, \qquad (1)$$

where $\gamma(\vec{p})$ is the momentum density distribution of electrons in the target [17]. The moments of the electron momentum density sample the interior as well as exterior regions of the EMD and are defined as

$$\langle p^n\rangle = 4\pi\int_0^{\infty} p^{n+2}\gamma(p)dp, \quad -2\leqslant n\leqslant 4. \qquad (2)$$

Here, $\gamma(p)$ is the *spherically averaged* momentum density. Some of these expectation values are also related to atomic properties, as follows: the $\langle p^{-1}\rangle$ moment is twice the peak value of the impulse profile $J(0)$, the $\langle p\rangle$ moment is empirically found to be almost proportional to the exact Hartree-Fock exchange energy [18], the $\langle p^2\rangle$ expectation value is proportional to the kinetic energy, the average value $\langle p^3\rangle$ is approximately proportional to the initial value of the Patterson function in crystallography [19,20], while the $\langle p^4\rangle$ moment occurs in the Breit-Pauli relativistic correction for the energy [21].

The momentum density in Eq. (1) is obtained in the present scheme from the Fourier transformed Kohn-Sham (KS) orbitals which, are solutions of the one-electron KS equations

$$\{-\nabla^2/2+v_{\text{eff}}(\vec{r})\}\psi_i(\vec{r})=\epsilon_i\psi_i(\vec{r}), \quad i=1,2,\ldots,N, \quad (3)$$

where

TABLE V. $\langle p^n\rangle$ moments for helium atom in different theories. The number in brackets denotes the power of 10.

Moments	BLYP	PW91	PBE	CAPZ	SICLDA
$\langle p^{-2}\rangle$	4.4169[0]	4.4036E[0]	4.4054E[0]	4.5040E[0]	3.9162E[0]
$\langle p^{-1}\rangle$	2.2083E[0]	2.2060E[0]	2.2070E[0]	2.2351E[0]	2.1042E[0]
$\langle p\rangle$	2.7746E[0]	2.7730E[0]	2.7700E[0]	2.7276E[0]	2.8337E[0]
$\langle p^2\rangle$	5.7478E[0]	5.7257E[0]	5.7119E[0]	5.5328E[0]	5.8362E[0]
$\langle p^3\rangle$	1.8600E[1]	1.8417E[1]	1.8346E[1]	1.7510E[1]	1.8393E[1]
$\langle p^4\rangle$	1.1311E[2]	1.1120E[2]	1.1052E[2]	1.0425E[2]	1.0789E[2]

TABLE VI. $\langle p^n \rangle$ moments for argon atom in different theories.

Moments	BLYP	PW91	PBE	CAPZ	SICLDA
$\langle p^{-2} \rangle$	1.3260E[1]	1.3179E[1]	1.3174E[1]	1.3260E[1]	1.2988E[1]
$\langle p^{-1} \rangle$	1.0179E[1]	1.0154E[1]	1.0155E[1]	1.0180E[1]	1.0090E[1]
$\langle p \rangle$	8.8672E[1]	8.8685E[1]	8.8662E[1]	8.8671E[1]	8.8932E[1]
$\langle p^2 \rangle$	1.0538E[3]	1.0537E[3]	1.0533E[3]	1.0539E[3]	1.0563E[3]
$\langle p^3 \rangle$	2.4298E[4]	2.4292E[4]	2.4285E[4]	2.4356E[4]	2.4335E[4]
$\langle p^4 \rangle$	1.9185E[6]	1.9174E[6]	1.9160E[6]	1.3312E[6]	1.3514E[6]

$$v_{\text{eff}}(\vec{r}) = -Z/r + \int n(\vec{r}')/|\vec{r}-\vec{r}'|d^3r' + \mu_{xc}(\vec{r}).$$

Different prescriptions are employed for μ_{xc}, the exchange-correlation part of the potential. The local-density calculations are carried out using the Ceperley-Alder [22] homogeneous electron gas data as parametrized by Perdew and Zunger (CAPZ) [23]. It has been pointed out by Lam and Platzman [24] that the above prescription of the EMD calculation requires a correction for the correlation effects beyond the independent electron approximation. Estimates of this correction for the Compton profiles (CP's) have been obtained [25,26] and are found to be marginal. But it could be important especially for the higher moments of EMD. The present paper which is basically a comparative study of Compton profiles ignores this correction.

The spherically averaged Compton profiles have been calculated for He, Ne, Ar, and Kr atoms. The choice of inert atomic systems was due to availability of experimental CP's for comparison. The KS orbitals are obtained from the Herman and Skillman [27] atomic structure code, which are then Fourier transformed using an accurate *Filon* routine. The normalization of EMD was correct at least up to six significant figures. We, however wish to note that the $\langle p^4 \rangle$ moment is sensitive to the choice of p mesh. The calculated Compton profiles along with their available accurate theoretical and experimental counterparts are presented in Tables I–IV while $\langle p^n \rangle$ moments of the EMD are given in Tables V–VIII. The Compton profiles within LDA and various GGA schemes are, in general, higher than the experimental CP at and around $q=0$. They cross each other typically in the q range 0.6 a.u. to 1.0 a.u., and are in good agreement in the asymptotic region. In case of Helium atom, CP's within different GGA schemes are in good agreement and are closer to the experimental CP in the *low q* region when compared against the LDA counterpart. For Ne, Ar, and Kr, in the low q region, the Compton profile within the BLYP scheme lies between its LDA and PBE and PW91 counterparts. Thus, amongst various GGA's, BLYP functional provides the least improvement over LDA Compton profile, in fact, in the case of Kr, CP in BLYP approximation is slightly higher than LDA CP. The higher values of CP near the origin in LDA and BLYP indicate localization of electron momentum density in the vicinity of $q=0$. This observation also comes from $\langle p^{-1} \rangle$ and $\langle p^{-2} \rangle$ moments of the electron momentum density. These moments are larger in LDA and BLYP approximations. It is also evident that CP values within the PW91 and PBE approximations are practically identical. This however is not surprising as the PBE functional satisfies many formal properties of density-functional theory and is essentially a simplification of the PW91 functional. In case of neon, comparison of present calculations of Compton profiles and the moments of EMD against those obtained from accurate configuration interaction (CI) wave functions brings out the following facts: (i) PW91 and PBE functionals outperform BLYP, particularly for the $\langle p^{-1} \rangle$ and $\langle p^{-2} \rangle$ moments. (ii) Various GGA schemes provide good estimates of $\langle p \rangle$ and $\langle p^2 \rangle$ moments. Thus GGA seems to be sufficiently accurate for these moments. (iii) $\langle p^3 \rangle$ and $\langle p^4 \rangle$ moments are slightly overestimated, which is a consequence of normalization constraints. Thus it is seen that GGA does provide some improvement over LDA, however it is only marginal. This limited success of GGA could possibly be due to poor description of the valence region, that occurs due to the self-interaction effects, which are not corrected for in any of these GGA functionals. To verify this, we have also calculated Compton profiles and moments of EMD within a self-interaction corrected LDA scheme. The self-interaction correction was applied to the Coulomb and the exchange part following the Perdew-Zunger [23] procedure, while for the correlation the Gunnarsson-Lundquist [31] (LDA) prescription was used. The calculated self-interaction correction local-density approximation (SICLDA) Compton profiles are also included in Tables I–IV. It is evident from the tables that self-interaction correction significantly improves the

TABLE VII. $\langle p^n \rangle$ moments for neon atom in different theories.

Moments	BLYP	PW91	PBE	CAPZ	CI	SICLDA
$\langle p^{-2} \rangle$	5.7747E[0]	5.7437E[0]	5.7432E[0]	5.5527E[0]	5.4795E[0]	5.5369E[0]
$\langle p^{-1} \rangle$	5.5704E[0]	5.5583E[0]	5.5599E[0]	5.4782E[0]	5.4448E[0]	5.3589E[0]
$\langle p \rangle$	3.5104E[1]	3.5110E[1]	3.5093E[1]	3.5241E[1]	3.5197E[1]	3.5352E[1]
$\langle p^2 \rangle$	2.5738E[2]	2.5727E[2]	2.5712E[2]	2.5775E[2]	2.5709E[2]	2.5832E[2]
$\langle p^3 \rangle$	3.5984E[3]	3.5958E[3]	3.5941E[3]	3.5915E[3]	3.5843E[3]	3.5885E[3]
$\langle p^4 \rangle$	1.0068E[5]	1.0057E[5]	1.0050E[5]	9.8719E[4]	9.8596E[4]	1.0218E[5]

TABLE VIII. $\langle p^n \rangle$ moments for krypton atom in different theories.

Moments	BLYP	PW91	PBE	CAPZ	SICLDA
$\langle p^{-2} \rangle$	1.7433E[1]	1.7329E[1]	1.7332E[1]	1.7298E[1]	1.7106E[1]
$\langle p^{-1} \rangle$	1.4500E[1]	1.4468E[1]	1.4470E[1]	1.4465E[1]	1.4400E[1]
$\langle p \rangle$	2.8130E[2]	2.8133E[2]	2.8129E[2]	2.8115E[2]	2.8177E[2]
$\langle p^2 \rangle$	5.5021E[3]	5.5020E[3]	5.5010E[3]	5.4929E[3]	5.5094E[3]
$\langle p^3 \rangle$	2.2463E[5]	2.2462E[5]	2.2458E[5]	2.2393E[5]	2.2457E[5]
$\langle p^4 \rangle$	5.0522E[7]	5.0510E[7]	5.0784E[7]	5.0212E[7]	5.0305E[7]

Compton profile in the important low q region. The Compton profile within SICLDA formalism is also in better agreement with accurate CI than its LDA and GGA counterparts. It is also seen from Table IV that SICLDA formalism performs well for $\langle p^{-2} \rangle$, $\langle p^{-1} \rangle$, and also $\langle p^3 \rangle$ moments but tends to slightly overestimate the $\langle p \rangle$ and $\langle p^2 \rangle$ moments. The effect of SIC thus, is to push momentum density from the neighborhood of the origin to the intermediate q region. In SICLDA scheme, the exchange potential has the exact $-1/r$ asymptotic nature, as a result of which electrons in the valence region experience more attractive potential. The improvement observed in SICLDA CP's is a consequence of improved valence description of atomic systems and demonstrates its necessity in the study of Compton profiles. In the present paper we have ignored Lam-Platzman correction, which is necessary to capture correlation effects beyond the independent-particle model. Addition of this correction might further lower the Compton profile near the peak and improve the agreement with the experimental Compton profile but would not quantitatively change the observed trend.

To conclude, a comparative study of the Compton profiles and various moments of momentum density has been carried out within the most popular improvement schemes such as generalized gradient approximation and self-interaction correction. The results indicate that GGA provides little improvement over LDA and demonstrates the need of GGA functionals capable of providing good description of valence region for the study of momentum-space properties in localized systems. We believe that the conclusions drawn here would also hold in case of molecules.

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