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Brief Reports

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Electron density to electron momentum density: The use of an energy constraint

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A modification of the Burkhardt, Kónya, Coulson, and March (BKCM) procedure [Phys. Rev. A 24, 2906 (1981)], enabling an estimation of electron momentum density exclusively from the knowledge of an atomic electron density, has been presented. A known value of the electronic energy has been employed as a constraint in effecting this modification without loss of simplicity of the BKCM procedure. These electron momentum densities are seen to be more physical than their unmodified counterparts.

I. INTRODUCTION

In a recent article, Gadre and Pathak[1] have demonstrated, by means of certain semiclassical relationships, that it is possible to extract reasonable estimates of the atomic electron momentum density $\chi(\vec{p})$, starting from a coordinate-space atomic electron density $\rho(\vec{r})$. The procedure described in Ref. 1 hinges on the earlier studies by Burkhardt,[2] Kónya,[3] and Coulson and March[4] (abbreviated as the BKCM procedure). For a given spherically symmetric, strictly monotone decreasing atomic electron density $\rho(r)$, the direct BKCM scheme that enables one to estimate the momentum density $\chi(p)$ is based on the semiclassical relationship (in a.u.)

$$\rho(r)=p^3(r)/3\pi^2 \ , \tag{1}$$

$\rho(r)$ being the maximum momentum of an atomic electron at a distance r from the nucleus. A reverse transformation effecting $\chi(p)\rightarrow\rho(r)$, starting from a monotone decreasing $\chi(p)$, was also discussed in detail in Ref. 1, which is dictated by an analogous reciprocal relationship

$$\chi(p)=r^3(p)/3\pi^2 \ . \tag{2}$$

The transformations (1) and (2) are a consequence of the phase-space considerations which, in turn, are based upon the uncertainty relations (in a.u.)

$$\begin{aligned}&\Delta p_x\Delta x\gtrsim 2\pi \ ,\\ &\Delta p_y\Delta y\gtrsim 2\pi \ ,\\ &\Delta p_z\Delta z\gtrsim 2\pi \ .\end{aligned} \tag{3}$$

Note that these relations *are inequalities, not equations* and they are only true in an order-of-magnitude sense. However, when used as equations, they lead to the well-known Thomas-Fermi statistical atomic model wherein the BKCM transformations become exact. As an approximate procedure, the BKCM scheme qualifies to be a useful one,[1] especially within the realm of the density functional (DF) formalism[5] where, for electronic systems in their ground states, the electron density $\rho(\vec{r})$ is endowed with a status of a basic variable with no explicit reference to the ground-state many-particle wave function. Within DF, in principle, an exact transformation to obtain $\chi(\vec{p})$ from the knowledge of $\rho(\vec{r})$ was developed by Lam and Platzman.[6] However, in practice, one is restricted to their so-termed locally averaged method[6] (LAM) which was shown to be exactly identical to the direct BKCM procedure for spherically symmetric, monotone decreasing, densities $\rho(r)$.[7] Incidentally, the advantage of the BKCM technique over LAM is that the former is analytically simpler and enables one to transform from $\chi(p)\rightarrow\rho(r)$ in a straightforward manner. It is easily observed that the transformations (1) and (2) preserve the normalization, i.e.,

$$\int_0^\infty \rho(r)4\pi r^2\,dr=\int_0^\infty \chi(p)4\pi p^2\,dp \ .$$

Admittedly, the kinetic energy estimated from the momentum density $\chi(p)$ derived from an application of the direct BKCM technique does not match the exact kinetic energy T. However, in the work of Ref. 1, it has been proven that $\langle p^2/2\rangle$ extracted from the

$\chi(p)$ obtained by the direct BKCM procedure equals a definite ingredient of the kinetic energy, namely, the zeroth-order Thomas-Fermi contribution T_0 for atomic systems, i.e.,

$$\langle p^2/2\rangle \equiv \int_0^\infty \chi(p) 2\pi p^4\, dp = \tfrac{3}{10}(3\pi^2)^{2/3} \int \rho^{5/3}(r)\, d\tau = T_0 \ . \tag{4}$$

Another artifact of the BKCM procedure is that the $\chi(p)$ obtained is monotone decreasing with a singularity at the origin; this last characteristic is obviously unphysical. Also, while most atoms actually show a monotonic decreasing $\chi(p)$, there are instances such as the halogens and the inert elements for which this is not found to hold well.[8–10] Further, the $\chi(p)$ obtained from the BKCM technique is cut off at a finite value of the momentum[1] and, as such, the atom has a finite boundary in momentum space.

In this article, an attempt has been made to obtain more physical momentum densities with a modification of the direct BKCM procedure. An endeavor has been made to answer the question: Given the experimental or a good theoretical (e.g., near Hartree-Fock) spherically averaged density $\rho(r)$ and the corresponding total energy E, what can one say about the best possible estimate of the momentum density $\chi(p)$? Thus the known value of the kinetic energy T [$T=-E$ by the virial theorem for the given density $\rho(r)$] serves as an additional constraint. Thus the $\chi(p)$ must satisfy

$$\langle p^2/2\rangle \equiv \int_0^\infty \chi(p) 2\pi p^4\, dp = T = -E \ . \tag{5}$$

Section II demonstrates that this can be incorporated upon a modification of the BKCM procedure.

II. CONSTRAINED BKCM (*C*-BKCM) SCHEME

To introduce Eq. (5) as a constraint, the flexibility in the relations (3) could be harnessed. This may be brought about through a modification of the relationships (1) and (2) without losing the inherent simplicity of the BKCM transformations. One therefore has to answer the question: What are the more general, yet simple, transformations that would preserve the normalization *and* also lead to the known total kinetic energy? For this purpose, consider the transformations

$$\rho(r) = \frac{\alpha}{3\pi^2} p^n(r) \ , \tag{6}$$

$$\chi(p) = \frac{\alpha}{3\pi^2} r^n(p) \ . \tag{7}$$

With these, one has

$$\int \rho(r)\, d\tau = 4\pi \left(\frac{\alpha}{3\pi^2}\right) \int_{r=0}^{r=\infty} p^n(r) r^2\, dr = \frac{4\pi}{3}\left(\frac{3\pi^2}{\alpha}\right)^{(3-n)/n} \int_{p=\infty}^{p=0} d\{\chi^{3/n}(p)\} p^n$$

$$= \frac{4\pi}{3}\left(\frac{3\pi^2}{\alpha}\right)^{(3-n)/n} \left(\chi^{3/n}(p) p^n \Big|_\infty^0 + \int_{p=0}^{p=\infty} \chi^{3/n}(p)\, np^{n-1}\, dp \right) \ .$$

The integrated term vanishes for atomic densities (and finite, positive n) yielding

$$\int \rho(r)\, d\tau = \frac{n}{3}\left(\frac{3\pi^2}{\alpha}\right)^{(3-n)/n} \int_0^\infty \chi^{3/n}(p) 4\pi p^{n-1}\, dp \ , \tag{8}$$

which, in order that the normalization is preserved, demands uniquely that $n=3$ (note: the normalization requirement is independent of any positive, fixed value of α for a given atomic system). The freedom offered in the choice of α shall be exploited to constrain the resultant kinetic energy to its known value. Thus the modified BKCM equations yield

$$\rho(r) = \frac{\alpha}{3\pi^2} p^3(r) \ , \tag{6a}$$

$$\chi(p) = \frac{\alpha}{3\pi^2} r^3(p) \ , \tag{7a}$$

which define the constrained-BKCM (*C*-BKCM) transformations. With these relationships, the connection

$$\langle p^m\rangle_{C\text{-BKCM}} = \alpha^{-m/3} \langle p^m\rangle_{\text{BKCM}} \tag{9}$$

is obvious, so that the kinetic energies are linked through

$$\langle p^2/2\rangle_{C\text{-BKCM}} = \alpha^{-2/3} T_0 \ . \tag{10}$$

Therefore, by setting

$$\alpha = (T_0/T)^{3/2} \ , \tag{11}$$

$\langle p^2/2\rangle$ becomes equal to T, the actual known kinetic energy. Substitution of this value of α, less than unity, back into Eqs. (6a) and (7a) fully defines the *C*-BKCM technique, which (a) ensures the normalization, (b) engenders the correct total kinetic energy, and (c) renders the BKCM procedure atom dependent. Thus, by the virtue of these attributes, the *C*-BKCM scheme is expected to yield more physcial $\chi(p)$'s as compared to those derived through the application of the direct unmodified BKCM procedure. The next section demonstrates this with the help of the numerical tests carried out.

III. NUMERICAL TESTS AND DISCUSSION

In the spirit of purely testing the usefulness of *C*-BKCM transformation, the atoms $Z=3$–36 were

TABLE I. Atomic $\langle p^{-1} \rangle$ and $\langle p \rangle$ expectation values for a few cases within the BKCM, constrained BKCM schemes, compared with their Hartree-Fock counterparts. (See text for further details.)

Atom	$\langle p^{-1} \rangle$ (a.u.) BKCM	C-BKCM	HF	$\langle p \rangle$ (a.u.) BKCM	C-BKCM	HF
Li	6.83	6.48	5.19	4.77	5.03	4.91
N	6.60	6.24	5.60	18.06	19.10	18.86
Ne	6.26	5.99	5.46	34.66	36.21	35.20
Na	10.67	10.23	8.71	40.72	40.12	40.73
P	11.76	11.32	10.14	65.05	65.80	66.18
Cl	11.50	11.09	10.16	79.62	82.62	80.65
Ar	11.28	10.88	10.13	87.53	90.77	88.70
K	16.21	15.64	13.77	94.85	98.32	96.22
Cr	16.03	15.47	12.25	138.8	143.8	142.5
Ni	15.23	14.72	13.81	181.9	188.2	185.3
Br	15.98	15.50	14.40	265.8	274.0	268.9
Kr	15.83	15.36	14.48	278.4	286.9	281.4

taken for a scrutiny, employing the near Hartree-Fock densities derived from the tabulations by Clementi and Roetti,[11] with the corresponding total energies. One could have, of course, employed the actual experimental energy data. Table I displays $\langle p^{-1} \rangle$ and $\langle p \rangle$ values obtained via the BKCM, the C-BKCM procedures along with their near Hartree-Fock counterparts. A marked improvement throughout can be seen for the C-BKCM $\langle p^{-1} \rangle$ expectation values which are smaller than the corresponding BKCM values, and also that they are seen to better match the near Hartree-Fock ones. The C-BKCM $\langle p \rangle$ values are enhanced as compared to those obtained from the unmodified version as ex-

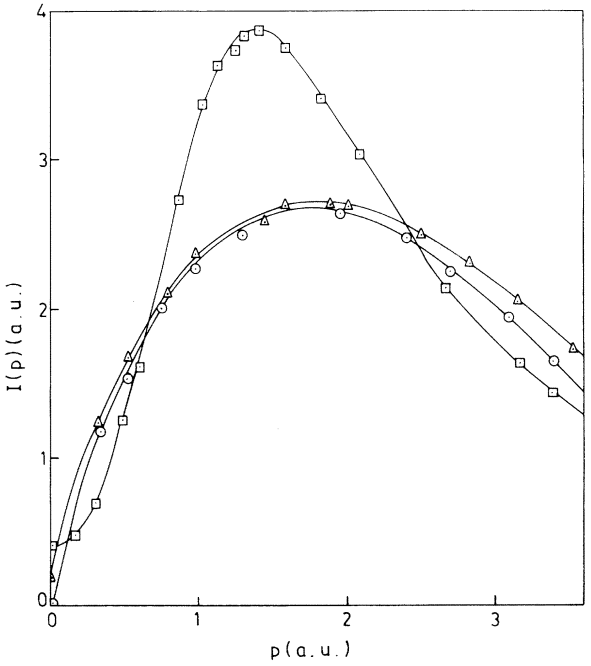

FIG. 1. Radial momentum densities for the neon atom employing —⊙—⊙—⊙— BKCM, —▲—▲—▲—▲— C-BKCM, and —⊡—⊡—⊡— near Hartree-Fock (NHF) procedures. The plots for the C-BKCM and NHF densities are shifted upwards by 0.2 and 0.4 units, respectively, for the sake of clarity. (See text for further details.)

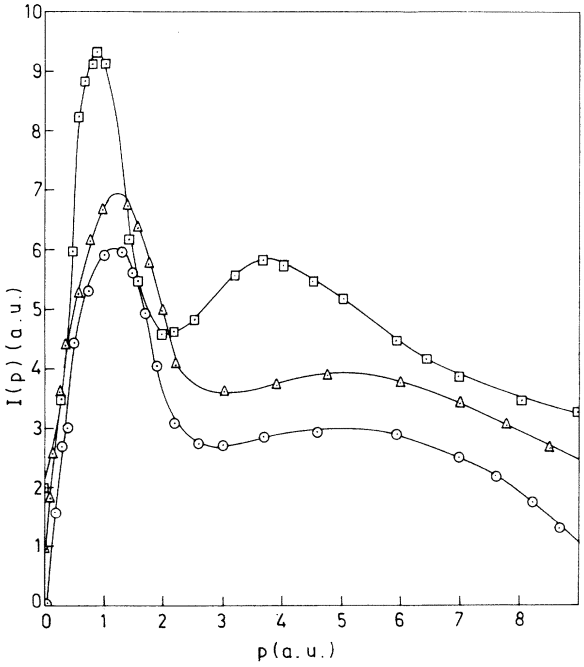

FIG. 2. Radial momentum densities for the krypton atom employing —⊙—⊙—⊙— BKCM, —▲—▲—▲— C-BKCM, and —⊡—⊡—⊡— near Hartree-Fock (NHF) procedures. The plots for the C-BKCM and NHF densities are shifted upwards by 1.0 and 2.0 units, respectively, for the sake of clarity.

pected [refer to Eq. (9)], and the correction to the latter was seen to be in the right direction even though the modified technique overestimates their near Hartree-Fock (NHF) counterparts a little. The following trends may be noticed:

$$\langle p^{-1}\rangle_{\mathrm{NHF}} < \langle p^{-1}\rangle_{C\text{-BKCM}} < \langle p^{-1}\rangle_{\mathrm{BKCM}}$$

and

$$\langle p\rangle_{\mathrm{BKCM}} < \langle p\rangle_{\mathrm{NHF}} < \langle p\rangle_{C\text{-BKCM}} \ .$$

A higher cutoff for the momentum densities obtained via the *C*-BKCM scheme, compared with the BKCM one, is yet another desirable feature. For instance, for the atoms Ne, Ar, and Kr, the cutoffs within the unmodified BKCM technique occur around 26, 48, and 97 a.u., whereas with the *C*-BKCM method it is seen to extend to around 28, 50, and 100 a.u. Thus, as has been stipulated, the momentum densities undergo an improvement on the whole, even though certain undesirable characteristics, viz., the singularity at the origin, a finite cutoff, and exclusively monotonic decreasing nature of $\chi(p)$, cannot be removed.

Another interesting observation is that the shells in momentum space, i.e., the maxima in the radial atomic momentum density $I(p)=4\pi p^2\chi(p)$, occur at nearly the same momentum values as the NHF ones for a given atomic system both for the unmodified as well as modified BKCM versions. This is evident from Figs. 1 and 2 for the cases Ne and Kr. It is noteworthy that both the BKCM procedures are seen to preserve the shell structure in momentum space.

Thus a simple modification of the BKCM procedure, with just a single experimental energy constraint imposed, is seen to lead to more physical atomic momentum densities.

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