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Transformation from metallic electron charge density to electron momentum density

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Abstract. There is no direct and exact relation between the electron charge density, $\rho(\boldsymbol{r})$, and electron momentum density, $\gamma(\boldsymbol{p})$. Two approximate methods for transforming from $\rho(\boldsymbol{r})$ to $\gamma(\boldsymbol{p})$ developed in the literature are briefly outlined, and these two methods are applied to metallic Al, V and Cu. The results are compared with each other and with experiment.

It is well known that in the case of the independent-particle approximation (IPA), the electron charge density (ECD), $\rho(\boldsymbol{r})$, of an N-particle system is obtained from the position-space single-particle wavefunctions $\Psi_j(\boldsymbol{r})$ by using the relation

$$\rho(\boldsymbol{r}) = \sum_{j}^{\text{occ}} |\Psi_j(\boldsymbol{r})|^2. \tag{1}$$

Similarly, the electron momentum density (EMD), $\gamma(\boldsymbol{p})$, can be obtained from

$$\gamma(\boldsymbol{p}) = \sum_{j}^{\text{occ}} |\varphi_j(\boldsymbol{p})|^2 \tag{2}$$

where the $\varphi_j(\boldsymbol{p})$ are the momentum-space single-particle wavefunctions. The two wavefunctions $\Psi_j(\boldsymbol{r})$ and $\varphi_j(\boldsymbol{p})$ are related to each other by the Dirac–Fourier transform (in atomic units)

$$\varphi_j(\boldsymbol{p}) = (2\pi)^{-3/2} \int \Psi_j(\boldsymbol{r}) \exp(-\mathrm{i}\boldsymbol{p}\cdot\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}. \tag{3}$$

The usual practice followed in the calculation of the EMD, $\gamma(\boldsymbol{p})$, is to obtain first the position-space wavefunctions Ψ_j in the IPA and then to calculate the corresponding momentum-space wavefunctions φ_j using (3). $\gamma(\boldsymbol{p})$, is then obtained from (2). $\gamma(\boldsymbol{p})$ thus determined forms the physical quantity of interest studied through the measurement of photon Compton profiles (CP) (Williams 1977, Cooper 1985):

$$J_{\hat{\boldsymbol{n}}}(q) = \int \gamma(\boldsymbol{p})\delta(q - \boldsymbol{p}\cdot\hat{\boldsymbol{n}})\, \mathrm{d}\boldsymbol{p} \tag{4}$$

where $\hat{\boldsymbol{n}}$ is a unit vector along the direction of the scattering vector $(\boldsymbol{k}_2 - \boldsymbol{k}_1)$, $\boldsymbol{k}_2$ and $\boldsymbol{k}_1$ being the wavevectors of the scattered and incident photon, respectively, in the Compton scattering process.

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There does not appear to be a method of obtaining $\gamma(\boldsymbol{p})$ from $\rho(\boldsymbol{r})$ (or $\rho(\boldsymbol{r})$ from $\gamma(\boldsymbol{p})$) accurately by using an exact formula. However, some recent calculations have demonstrated how $\gamma(\boldsymbol{p})$ can be estimated directly from knowledge of the ECD, $\rho(\boldsymbol{r})$, and these calculations have provided results that are in satisfactory agreement with the experimental CP data for atoms (Gadre and Pathak 1981, Parr *et al* 1986), molecules (Pathak *et al* 1984, Parr *et al* 1986) and metals (Mishra and Singru 1986, 1987).

It is well known from density functional theory (DFT) that given the ground-state ECD, $\rho(\boldsymbol{r})$, the external potential $V(\boldsymbol{r})$ is uniquely determined (Hohenberg and Kohn 1964). The ground-state wavefunction Ψ is thus also uniquely determined provided the ground state is non-degenerate, which is usually the case. This wavefunction, Ψ, then, in turn uniquely determines $\gamma(\boldsymbol{p})$ through a uniquely determined φ. Thus given any ground-state ECD, $\rho(\boldsymbol{r})$, it should be possible, *in principle*, to obtain corresponding $\gamma(\boldsymbol{p})$. However, as pointed out before, no such direct and exact relation transforming $\rho(\boldsymbol{r})$ into $\gamma(\boldsymbol{p})$ (or vice versa) is known. Recently we have applied two methods to transform from ECD to EMD in metals (Mishra and Singru 1986, 1987). Although these methods lead us to spherically symmetric EMD, they provide information that is useful in many cases. We give below a brief outline of these two *approximate* methods for transformation from ECD to EMD. The theoretical results of these methods have been compared with experiment and with each other for the first time and it has been shown that they provide reasonably good estimates of EMD derived from ECD.

One such approximate procedure for carrying out the above transformation is based on quasi-classical phase-space considerations and is named in the literature after its originators (Burkhardt 1936, Konya 1949, Coulson and March 1950). This method was later revived and developed by Gadre and Pathak (1981) whose group later applied it to several systems, and hence we shall refer to it as the BKCM-GP method. This method is exact only within the Thomas–Fermi theory.

The BKCM-GP method starts with a function $P_0(\boldsymbol{r})$ which is the maximum momentum that an electron can have while at the position $\boldsymbol{r}$ and is related to the density $\rho(\boldsymbol{r})$ at $\boldsymbol{r}$ by

$$P_0(\boldsymbol{r}) = (3\pi^2\rho(\boldsymbol{r}))^{1/3} \tag{5}$$

and the total EMD is then obtained by adding the contributions from different regions in the position space. It has been shown by Gadre and Pathak (1981) that for the case of the ECD, $\rho(\boldsymbol{r})$, decreasing monotonically with r, one can write the direct and reverse transformations as

$$\gamma(\boldsymbol{p}) = R^3(\boldsymbol{p})/3\pi^2 \tag{6}$$

$$\rho(\boldsymbol{r}) = P_0^3(\boldsymbol{r})/3\pi^2 \tag{7}$$

where R is the inverse of P_0.

The relations (6) and (7) have been used by Gadre and Pathak (1981) to transform from the ECD, $\rho(\boldsymbol{r})$, to the EMD, $\gamma(\boldsymbol{p})$, in the atomic systems Li, Be, B, C, N, O, F and Ne. These authors calculated the CP and the values of kinetic energy $\langle p^2/2\rangle$, $J(0)$ and $q_{0.5}$ for these atoms and compared these results with experiment. This comparison showed that their procedure yielded reasonable estimates of various quantities. In a subsequent paper (Gadre *et al* 1983a) the BKCM-GP procedure for carrying out the direct transformation $\rho(\boldsymbol{r}) \rightarrow \gamma(\boldsymbol{p})$ was shown to be identical to the locally averaged method of Lam and Platzman (1974). Similarly the scope of the BKCM-GP procedure was extended to molecular densities (Pathak *et al* 1984). Later it was shown that the introduction of

energy constraints improved the agreement between the BKCM-GP theory and experiment (Gadre *et al* 1983b).

The BKCM-GP procedure has recently been extended to metallic systems by Mishra and Singru (1986). These authors have obtained $\gamma(\boldsymbol{p})$ from the spherically symmetric $\rho(\boldsymbol{r})$ calculated for metals by Moruzzi *et al* (1978) using band-structure methods. The results of $\gamma(\boldsymbol{p})$ so obtained were used to calculate the CP $J(q)$, and the expectation values $\langle p^n \rangle$ in metallic Li, Na, Al, Sc, V, Ti, Fe, Ni and Cu, and the agreement with experiment has been found to be satisfactory.

We now outline another method to obtain the EMD, $\gamma(\boldsymbol{p})$, from the ECD, $\rho(\boldsymbol{r})$, *via* a phase-space function, $f(\boldsymbol{r}, \boldsymbol{p})$, defined in the joint position and momentum space. This approach is based on the rigorous phase-space formalism, which is described in detail in the literature (Hillery *et al* 1984, Balazs and Jennings 1984). The phase-space function, $f(\boldsymbol{r}, \boldsymbol{p})$, is also known as Wigner's function and it obeys the following properties for a one-particle Wigner function:

$$\int f(\boldsymbol{r}, \boldsymbol{p})\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{p} = N \tag{8}$$

$$\int f(\boldsymbol{r}, \boldsymbol{p})\, \mathrm{d}\boldsymbol{p} = \rho(\boldsymbol{r}) \tag{9}$$

$$\int f(\boldsymbol{r}, \boldsymbol{p})\, \mathrm{d}\boldsymbol{r} = \gamma(\boldsymbol{p}). \tag{10}$$

The expectation value of the kinetic energy operator is obtained from

$$\langle T \rangle = \int (p^2/2m) f_1(\boldsymbol{r}, \boldsymbol{p})\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{p}. \tag{11}$$

It is observed from the above that the EMD, $\gamma(\boldsymbol{p})$ can be obtained from (10) if we know $f(\boldsymbol{r}, \boldsymbol{p})$. Parr *et al* (1986) combined the maximum-entropy principle with the above approach to determine $f(\boldsymbol{r}, \boldsymbol{p})$ in atoms and molecules, so that the properties in momentum space could be calculated in such a way as to obtain good agreement with experiment.

Following a similar approach we can obtain Wigner's function in metals (Mishra and Singru 1987)

$$f(\boldsymbol{r}, \boldsymbol{p}) = (3\rho/4\pi t)^{3/2} \rho(\boldsymbol{r}) \exp(-3\rho p^2/4t) \tag{12}$$

where $\rho = \rho(\boldsymbol{r})$ is the ECD and $t = t(\boldsymbol{r})$ is kinetic energy density given in $\boldsymbol{r}$-space by

$$t(\boldsymbol{r}) = \tfrac{3}{10}(3\pi^2)^{2/3}(\rho(\boldsymbol{r}))^{5/3} + \tfrac{1}{72}(\nabla\rho(\boldsymbol{r}))^2/\rho(\boldsymbol{r}) \tag{13}$$

where the second term is the Weizäcker correction term. We point out here that in our previous report we used a numerical coefficient of $\frac{1}{8}$ in the second term of (13). It has been pointed out in the literature (Kirznits 1957, March 1983) that this numerical coefficient should really be $\frac{1}{72}$ for better accuracy. We have therefore repeated our calculations using the numerical coefficient $\frac{1}{72}$ in (13). We find that a value of $\frac{1}{72}$ for the coefficient provides better agreement with the total kinetic energy. The starting point of our calculations for metals was the ECD, $\rho(\boldsymbol{r})$, reported by Moruzzi *et al* (1978) from which $t(\boldsymbol{r})$ and $f(\boldsymbol{r}, \boldsymbol{p})$ were calculated. $\gamma(\boldsymbol{p})$ was obtained from (15) using the $f(\boldsymbol{r}, \boldsymbol{p})$ so obtained. Theoretical values of the CP, and $\langle p^n \rangle$ obtained from these calculations, have been compared with experiment and found to show satisfactory agreement (Mishra and Singru 1987).

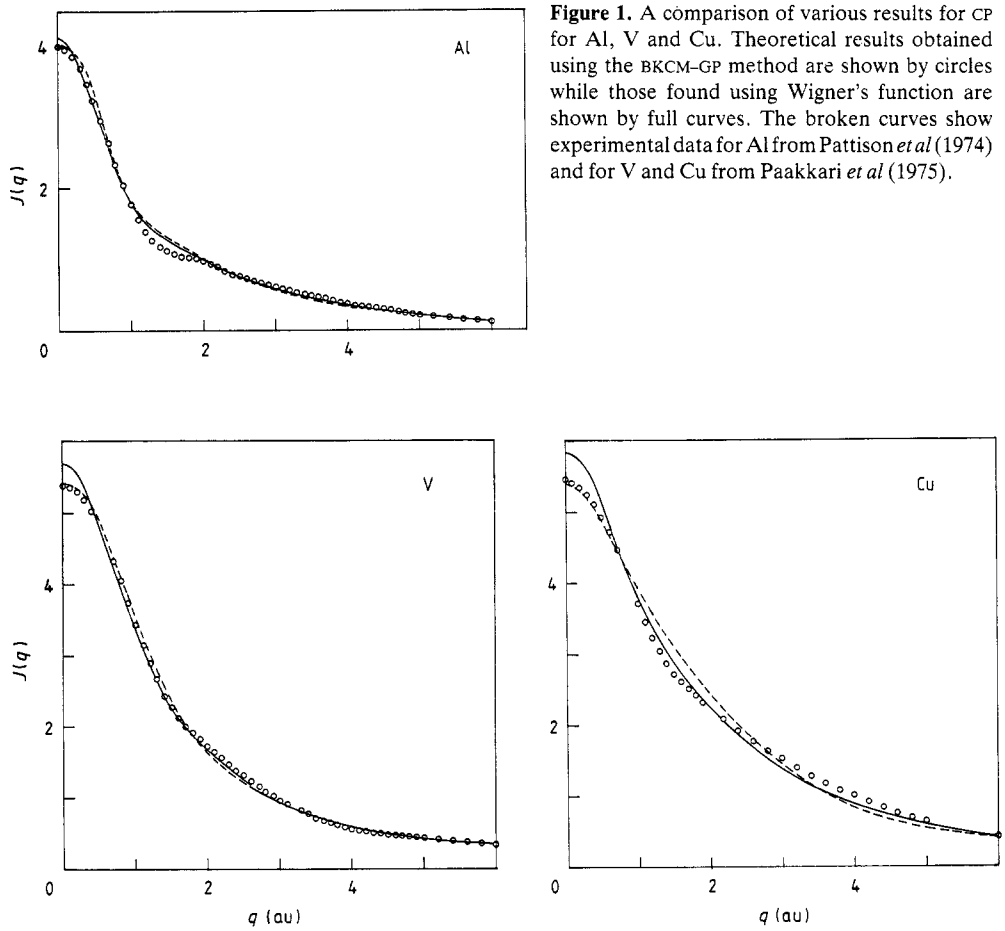

Figure 1. A comparison of various results for CP for Al, V and Cu. Theoretical results obtained using the BKCM-GP method are shown by circles while those found using Wigner's function are shown by full curves. The broken curves show experimental data for Al from Pattison *et al* (1974) and for V and Cu from Paakkari *et al* (1975).

To illustrate the degree of success obtained using the above two methods in metals we show in figure 1 a comparison between the CP obtained for metallic Al, V and Cu from (i) the BKCM-GP procedure, (ii) Wigner's phase-space function and (iii) experiment. These results are encouraging and they suggest that such methods could also have useful applications in the theory of positron annihilation. Such work is now in progress.

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