Electron Momentum Densities Near Zero Momentum

Ajit J. Thakkar and Amlan K. Roy

Department of Chemistry, University of New Brunswick
Fredericton, NB E3B 6E2, Canada
email: ajit@unb.ca
Web: http://www.unb.ca/chem/ajit/

The electron density $\rho(\vec{r})$ and the electron momentum density $\Pi(\vec{p})$ offer two different views of electronic structure. Many years ago, Coulson observed that $\rho(\vec{r})$ and $\Pi(\vec{p})$ are reciprocal in the sense that the valence region corresponds to large distances $r = |\vec{r}|$ and small momenta $p = |\vec{p}|$. Much attention has been paid to the small momentum behavior of the electron momentum density because of the importance of the valence region to chemistry.

Most experiments yield only the spherically averaged momentum density

$$\Pi_0(p) = (4\pi)^{-1} \int \Pi(\vec{p})\, \mathrm{d}\Omega_{\vec{p}}.$$

One way to focus on the small momentum behavior is by considering the leading terms of the MacLaurin expansion:

$$\Pi_0(p) = \Pi_0(p) + \frac{1}{2}\Pi_0''(0)\, p^2 + \frac{1}{4!}\Pi_0^{(4)}(0)\, p^4 + \cdots$$

where only even powers of p appear because of the inversion symmetry of the momentum density. The coefficients have been extracted from experimental Compton profiles for both atoms and molecules. Ab initio calculations including varying amounts of electron correlation have been reported [1-3]. Recent work [3] suggests that basis set effects are rather large. A calibration study on diatomic molecules using the fully numerical Hartree-Fock method developed by Laaksonen, Pyykkö, and Sundholm is reported in celebration of Pekka Pyykkö's 60th birthday.

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