SELF-CONSISTENT LCAO LOCAL DENSITY DETERMINATION OF ANISOTROPIC COMPTON PROFILE AND X-RAY STRUCTURE FACTORS IN DIAMOND *

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Our newly developed fully Self-Consistent Numerical Discrete Variational Method (which exactly treats all non-spherical parts of the crystal potential) yields X-ray scattering factors and anisotropies in the Compton profile of diamond in very good agreement with experiment.

Considerable interest exists in the predictions of the local density formalism (LDF) [1] on the ground state properties of solids, e.g. cohesive energies [2], X-ray form factors [3, 4] and Compton profiles [5]. LDF based calculations are usually beset with the difficulties of solving self-consistently the associated one-particle equation characterized by a *multi-center* non-spherical potential and hence, a variety of approximations have been introduced to reduce the complexity of the problem, LCAO-type calculations [4, 5] have overcome the difficulty of treating non-muffin-tin potentials and have demonstrated that efficient convergence with respect to the size of the basis set [4] can be obtained. However, the problem of carrying this type of calculation or self-consistency (SC) still remains a formidable task. Although these methods are capable of yielding reasonable results for the eigenvalues, an accurate evaluation of ground state functionals of the electron density is still non-trivial.

In this paper we apply our newly developed [6] self-consistent numerical discrete variational method (DVM) [7] to study the X-ray scattering factors and directional Compton profile for diamond. All non-spherical parts of the crystal potential are treated exactly using an efficient numerical LCAO basis set and a numerical Diophantine integration scheme. Local density exchange and correlation are incorporated directly into the crystal potential and full self-consistency is obtained. The resulting X-ray form factors are in good agreement with experiment [8, 9]

and with previous Hartree–Fock calculations [10]. While the non-SC Compton profile is too high at low momenta and lacks some high momentum components, the fully self-consistent results agree very well with experiment. Unlike the Hartree–Fock results, the anisotropy of the profile is found to be in reasonable agreement with experiment.

For the crystal problem, the general potential is given by

$$V(r) = V_{coul}(r) + F_{ex}[\rho_{sup}(r)] + F_{corr}[\rho_{sup}(r)] \qquad (1)$$

with the exchange, F_{ex}, and correlation, F_{corr}, potentials given in terms of the local density functions written in terms of superposed overlapping atomic densities, $\rho_{sup}(r)$. We use the free-electron $\rho^{1/3}$ exchange potential for F_{ex} and the correlation energy functional of Singwi et al. [11] as fitted to analytic form by Hedin and Lundqvist [12]. We do not spherically average $V(r)$ or linearize the local density functionals. The crystal wave functions $\psi_j(K, r)$ are expanded in terms of Bloch functions $\Phi_\mu^\alpha(K, r)$ [which are given in terms of LCAO basis orbitals χ_μ^α]. Unlike previous efforts which used simple analytic basis functions to overcome difficulties in calculating many-center integrals appearing in matrix elements (ME) of $V(r)$, we are able to exploit the variational efficiency of accurate *numerical* basis functions because we do not employ any analytic algorithms for calculating ME. Thus our $\chi_\mu^\alpha(r)$ are determined as numerical solutions of the atomic potential equivalent of eq. (1). Details of the method, and evidence for the variational superiority of even a minimal set (e.g., 1s, 2s and 2p) to a double-zeta Slater basis are given elsewhere