

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

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

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, $\rho_{\text{sup}}(\mathbf{r})$. 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 $V(\mathbf{r})$ or linearize the local density functionals. The crystal wave functions $\psi_j(\mathbf{K}, \mathbf{r})$ are expanded in terms of Bloch functions $\Phi_{\mu}^{\alpha}(\mathbf{K}, \mathbf{r})$ [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 $V(\mathbf{r})$, 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 $\chi_{\mu}^{\alpha}(\mathbf{r})$ 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

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[6], as is a full description of the method of obtaining crystal solutions. An extended numerical set of 1s, 2s, 2p, 3s and 3p are used in this study.

The initial guess for the ground state crystal density in our SC procedure is the population-dependent overlapping-atomic model in which $\rho_{\text{sup}}(\mathbf{r})$ is constructed as a lattice sum of atomic $\rho_{\alpha}(\mathbf{r})$ obtained from the numeric SC solution for atom α . With this model density, the superposition Coulomb potential $V_{\text{coul}}^{\text{sup}}(\mathbf{r})$ is a sum of one-site Coulomb potentials derived from $\rho_{\alpha}(\mathbf{r})$ by solving Poisson's equation.

Self-consistency is treated in two stages: in stage one, we perform a charge and configuration self-consistent (CCSC) calculation by recomputing $\{\chi_{\mu}^{\alpha}(\mathbf{r})\}$ and potential $V(\mathbf{r})$ on the basis of a new set of population numbers so as to minimize, in a least-squares sense, the deviation σ^2 between the input $\rho_{\text{sup}}(\mathbf{r})$ and the crystal density, $\rho_{\text{cry}}(\mathbf{r})$:

$$\Delta\rho(\mathbf{r}) \equiv \rho_{\text{cry}}(\mathbf{r}) - \rho_{\text{sup}}(\mathbf{r}), \quad \sigma^2 = \frac{1}{\Omega} \int \Delta\rho(\mathbf{r}) d\mathbf{r}. \quad (2)$$

We thus optimized our basis set *non-linearly* (by recomputing it at each step) so as to allow the $\chi_{\mu}^{\alpha}(\mathbf{r})$ to relax to the form of the iterated $\rho_{\text{cry}}(\mathbf{r})$. In the second stage (full self-consistency), we expand the residual $\Delta\rho(\mathbf{r})$ obtained at the last CCSC iteration in a Fourier series and compute the correction to the Coulomb potential due to this $\Delta\rho(\mathbf{r})$ as:

$$\Delta V_{\text{coul}}(\mathbf{r}) = -4\pi \sum_{\mathbf{K}_s \neq 0} K_s^{-2} \Delta\rho(\mathbf{K}_s) \exp(i\mathbf{K}_s \cdot \mathbf{r}). \quad (3)$$

Here $\Delta\rho(\mathbf{K}_s)$, the Fourier components of $\Delta\rho(\mathbf{r})$, are also calculated by a direct three-dimensional Diophantine integration. Note that since $\Delta\rho(\mathbf{r})$ cannot be expanded in terms of one-site densities located at the atomic sites it has been neglected in most of the previously published SC methods. Because of the smooth character of $\Delta\rho(\mathbf{r})$ (the main localized features near the core regions having been absorbed into $\rho_{\text{sup}}(\mathbf{r})$ in the CCSC step), only the first few \mathbf{K}_s vectors need to be considered in eq. (3) in order to converge the sum – a feature not shared by methods that treat the full (core + valence) density in a Fourier representation [4, 5]. To the correction $\Delta V_{\text{coul}}(\mathbf{r})$ we add $V_{\text{coul}}^{\text{sup}}(\mathbf{r})$ obtained at the previous iteration and the exchange and correlation potentials calculated from $\rho_{\text{cryst}}(\mathbf{r})$ and repeat the solution until the changes in $\Delta\rho(\mathbf{K}_s)$ between successive iterations are smaller

than 10^{-4} . Only the first 6 to 12 \mathbf{K}_s vectors and 2–4 iterations were needed to converge the SC cycle to this accuracy. The crystal density is computed at each iteration step by sampling the 6-nearest volume \mathbf{K} -points in the fcc Brillouin zone.

The final charge density is used to compute the X-ray form factors of diamond, shown in table 1 along with the experimental values [8, 9] and the crystalline Hartree–Fock (HF) results obtained with a Gaussian s/p basis set [10]. Our results using the exchange and correlation functionals agree quite closely with the experimental data (an experimental error of 1 to 5 per cent has been estimated). The deviations between our results, or the H-F results, from experiment are a non-systematic function of (h, k, l) – contrary to previous conclusions [3, 13]. The iterations towards SC improve the agreement with experiment quite considerably as is seen particularly for the “forbidden” reflection f_{222} .

The momentum density is calculated using the Fourier transformed Bloch function $\Phi_{\mu}^{\alpha}(\mathbf{p})$. The Compton profile $J(q)$ is computed in the impulse approximation from the Kubic Harmonics expansion of the momentum density [14] ($l_{\text{max}} \leq 12$). Table 2 summarizes and compares our results for the Compton profile $J(q)$ in the [100] direction to experiment [15, 16] and to the HF results [17]. Upon iterating our results to SC, $J(q)$ is lowered at low q and additional contributions start to appear at high q . We note that our non-SC results (with $\alpha = 2/3$ and correlation) are close to the non-SC analytic Slater basis DVM results of Seth and Ellis [18] (but with $\alpha = 0.70$ and no correlation). Similar increases in the form factors at low $[hkl]$ (table 1) upon iteration indicates some build-up in the bonding charge relative to the super-

Table 1
Experimental and calculated X-ray scattering factors for diamond with $f(0, 0, 0) = 6.0$.

hkl	first iteration	last iteration	exp [8] results	HF [10] results
111	3.071	3.281	3.32	3.29
220	1.982	1.995	1.98	1.93
311	1.792	1.692	1.66	1.69
222	0.0	0.139	0.14 [9]	0.08
400	1.531	1.493	1.48	1.57
331	1.510	1.605	1.58	1.55

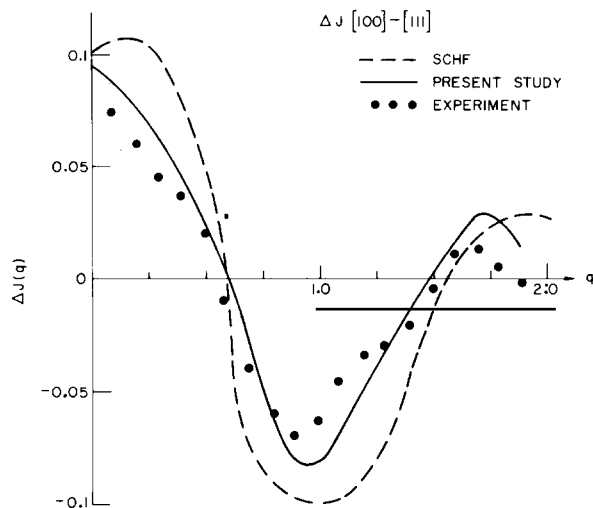


Fig. 1. Anisotropy of the [100]–[111] $J(q)$ in diamond compared with the self consistent Hartree–Fock [SCHF] results [17] and experiment [15].

position model. The HF results shown in table 2 indicate a lack of sufficient high momentum components and an overestimate of the profile at low q . Thus our full SC procedure accounts reasonably well for the charge redistribution in going from the atomic superposition to the crystalline results.

Fig. 1 shows the calculated [100]–[111] anisotropy of $J(q)$ in diamond and a comparison with the SCHF predictions and experiment. Our results do not peak at low q values; at higher q values, the anisotropy is considerably lower than that predicted by the HF theory. Some possible structure in the experimental data at $q \approx 1.0$ au is absent in both calculations.

The overall agreement of our results with experiment for both X-ray scattering factors and the Compton profile gives us some confidence as to the adequacy of our numerical basis set and self-consistency procedure. Although the eigenvalues of the local density one-particle equation (band structure) in diamond change only very little by adding the correlation potential and employing a full SC procedure, both the Compton profile and the total ground state energy are considerably affected by these effects – as will be discussed in more detail elsewhere.

Table 2
Experimental and calculated Compton profile in diamond in the [100] direction.

(au)	first iteration	last iteration	exp [15] results	exp [16] results	HF [17] results
0.0	2.19	2.05	2.09	2.08	2.18
0.2	2.17	2.01	2.07	2.06	2.15
0.4	2.06	1.93	1.91	1.94	2.05
0.6	1.84	1.75	1.73	1.79	1.84
0.8	1.57	1.52	1.46	1.55	1.55
1.0	1.20	1.28	1.10	1.29	1.22
1.2	0.87	0.96	0.86	0.94	0.88
1.6	0.46	0.48	0.47	0.45	0.46
2.0	0.31	0.33	–	0.31	0.29
3.0	0.15	0.19	–	0.18	–
4.0	0.08	0.11	–	0.10	–
5.0	0.04	0.06	–	0.06	–

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