Correlation Effects in the Compton Profile of Silicon

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Ab initio nonlocal pseudopotential variational quantum Monte Carlo techniques are used to compute the correlation effects on the valence momentum density and Compton profile of silicon. Our results for this case are in excellent agreement with the Lam-Platzman correction computed within the local density approximation. Within the approximations used, we rule out valence electron correlations as the dominant source of discrepancies between calculated and measured Compton profiles of silicon.
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The Compton effect [1] has been a very early test of the predictions of the quantum theory of solids [2]. With the advent of new, very high resolution Compton spectroscopy [3–8] there is renewed interest in this experimental technique as a probe of the detailed electronic structure of real materials [9].

Crystalline silicon, as one of the technologically most important and best studied materials, is an ideal test system to consider. Silicon momentum densities and Compton profiles have been studied experimentally with various techniques such as synchrotron radiation x-ray scattering [10,11], γ-ray scattering [12–16], and angular correlation of positron annihilation [17–19]. There have also been many theoretical computations of these quantities, ranging in complexity from tight-binding [20], empirical pseudopotential [21] to *ab initio* pseudopotential [22] and all-electron methods [23,24]. All calculations to date have relied on single-particle band theory in their interpretation of momentum densities and Compton profiles.

While the existing theoretical calculations are in close agreement with experimental observations, discrepancies remain to be explained. In particular, it is found that theoretical Compton profiles are too high at $\mathbf{q} = 0$ as compared to experiment in materials ranging from lithium [7] to silicon [9]. One possible source for such discrepancies is electron correlation beyond the single-particle approximation. In this Letter we develop the nonlocal pseudopotential variational quantum Monte Carlo (VQMC) method for momentum densities, and apply it to study the electron correlation effects on the Compton profile of silicon.

In the VQMC method, the true many-body state is approximated by

$$\Psi = \Psi_J d^{\uparrow} d^{\downarrow},$$

where the d are Slater determinants of single-particle orbitals ϕ_i such as the eigenstates of the Kohn-Sham equations [25,26]. We generate the single-particle orbitals by performing density functional theory (DFT) calculations in the local density approximation (LDA), using the Perdew-Zunger [27] parametrization of the Ceperley-Alder [28] exchange-correlation potential. Correlation effects are included into our many-body wave function via the Jastrow factor Ψ_J. The exact form of the Jastrow factor is determined variationally. Following Fahy, Wang, and Louie [29], we only include single- and two-particle terms:

$$\Psi_J(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \exp\left(\sum_i \chi(\mathbf{r}_i) - \sum_{i<j} u(|\mathbf{r}_i - \mathbf{r}_j|) \right).$$

The two-particle term u incorporates the correlations resulting from the Coulomb repulsion between electrons. It consists of two terms, $u_\sigma = u_\sigma^P + u_\sigma^{\text{var}}$. The σ index takes the values $\sigma = \uparrow\uparrow$ or $\uparrow\downarrow$, i.e., a different two-particle term applies between parallel and antiparallel spins. The usual plasmon term $u_\sigma^P(r) = \frac{A}{r}\left[1 - \exp(\frac{r}{F_\sigma})\right]$ is constructed to have the correct asymptotic dependence at $\mathbf{r} \to \infty$ and to satisfy the cusp condition at $\mathbf{r} \to 0$. A is treated as a single variational parameter in this term [29].

We introduce further variational freedom into the two-particle term via u^{var}. u^{var} is the most general polynomial expression on the interval $[0, L_0]$ that satisfies the conditions (1) $u'(0) = 0$, (2) $u(L_0) = 0$, and (3) $u'(L_0) = 0$ [30]. The first condition ensures that the cusp condition remains satisfied. Conditions (2) and (3) ensure that u and its derivative remain continuous at the cutoff radius L_0. This is necessary to avoid singularities in the kinetic energy of the wave function. The cutoff radius L_0 is chosen to be large enough so that the variational freedom in u^{var} can effectively influence the shape of the Coulomb hole. This means that L_0 should be chosen to be on the order of a few average electron-electron separations. Since the average r_s in silicon is 2, L_0 was chosen to be 15 a.u. We have used polynomials up to order 12, which corresponds to 18 variational parameters in this term.

As the two-particle term u has the effect of making the electrons avoid each other beyond what is dictated by the antisymmetry of the wave function, the u term alone tends to smooth the charge density [29]. The single-particle part χ of the Jastrow factor introduces variational freedom that allows adjustment of the charge density to further minimize the energy or the variance of the energy.

In our study we used the χ term in two ways: First, χ can be treated as a fully variational part of the wave function with no constraints. We used up to nine parameters (nine independent Fourier coefficients) in our study. This variational χ-factor will be referred to as χ^{var} in the following.

Second, χ can be used to restore the DFT charge density following the prescription of Ref. [29]. In the rest of this Letter the notation χ^{CD} will refer to this choice. In this case, χ is chosen to be $\chi^{\text{CD}}(\mathbf{r}) = \frac{1}{2} C \ln(\frac{\rho_{\text{LDA}}(\mathbf{r})}{\rho_{u\,\text{only}}(\mathbf{r})})$, where C is treated as a single variational parameter.

The optimal parameters in the Jastrow factor are determined via minimizing the variance of the total energy [30]. We estimate the variance of the total energy as

$$\sigma^2 = \frac{1}{\sum_j w(\mathbf{R}_j)} \sum_i \frac{(\hat{H} - E_T)^2 \Psi(\mathbf{R}_i)}{\Psi(\mathbf{R}_i)} w(\mathbf{R}_i),$$

where $\hat{H}$ is the Hamiltonian operator, and $\{\mathbf{R}_i\}$ is a set of N-electron configurations having probability distribution $|\Psi_{\text{guide}}(\mathbf{R}_i)|^2$. Ψ_{guide} is our best estimate of the optimal wave function and E_T is our best estimate for the ground-state energy. The weighting factors

$$w(\mathbf{R}_i) = \frac{|\Psi(\mathbf{R}_i)|^2}{|\Psi_{\text{guide}}(\mathbf{R}_i)|^2}$$

are required because the $\mathbf{R}_i$ are distributed with probability density $|\Psi_{\text{guide}}(\mathbf{R}_i)|^2$ and not with probability density $|\Psi(\mathbf{R}_i)|^2$. This formalism allows us to minimize σ^2 with respect to the variational parameters in the Jastrow factor on a *fixed* set of configurations, thus eliminating statistical noise from the minimization procedure. In practice, the variance minimization is carried out iteratively, i.e., the $\{\mathbf{R}_i\}$ are regenerated several times. The variance minimization and all subsequent calculations are carried out in a 16-atom (64-electron) simulation cell.

Table I shows the effect of introducing variational freedom in the wave function on the total energy. While most of the energy gain is realized with the simple 1-parameter plasmon term u^P [29], the introduction of further variational freedom lowers the energy further appreciably. Similar gains have been reported for Ge by Williamson *et al.* [30].

Once the optimal parameters have been determined, we turn to calculating the momentum density. The

TABLE I. Effect of the variational freedom in the Jastrow factor on the total energy of Si. The no-Jastrow-factor energy was set to zero. In parentheses are the estimates of the statistical error in the last digit.

Jastrow factor	Energy gain (eV/atom)
None	0.00(7)
u^P	$-3.10(5)$
$u^P + \chi^{\text{CD}}$	$-3.23(4)$
$u^P + \chi^{\text{var}}$	$-3.45(4)$
$u^P + u^{\text{var}} + \chi^{\text{var}}$	$-3.59(4)$

momentum density for a many-body system is given by the expression

$$N(\mathbf{k}) = \int d\mathbf{s}\, d\mathbf{r}_1 \cdots d\mathbf{r}_{N_e}$$
$$\times \Psi^*(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) e^{i\mathbf{k}\cdot\mathbf{s}} \Psi(\mathbf{r}_1 + \mathbf{s} \cdots \mathbf{r}_{N_e}),$$
$$= (N_{\text{conf}})^{-1} \sum_i^{N_{\text{conf}}} \int d\mathbf{s}\, e^{i\mathbf{k}\cdot\mathbf{s}} \Psi(\mathbf{R}_i + \mathbf{s})/\Psi(\mathbf{R}_i),$$

where the $\{\mathbf{R}_i\}$ are configurations generated with probability density $|\Psi(\mathbf{R}_i)|^2$. At each configuration the remaining three-dimensional integration is carried out directly on a uniform, randomly shifted grid. In our study this uniform grid was chosen to have $3 \times 3 \times 3$ points. Our method mirrors that of Ref. [31] used to sample pair correlation functions.

In general, converged momentum distributions require large k-point grids for the LDA calculation [22]. A dense k-grid corresponds to a large supercell simulation. Since doing a large supercell calculation is computationally prohibitive within VQMC, we do small supercell calculations with *generalized* periodic boundary conditions. In this scheme, the many-body wave function is required to have the property

$$\frac{\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_i + \mathbf{L}, \ldots, \mathbf{r}_{N_e})}{\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_i, \ldots, \mathbf{r}_{N_e})} = e^{i\mathbf{K}\cdot\mathbf{L}},$$

where $\mathbf{L}$ is a lattice vector of the *simulation* cell and the phase factor $\Phi = e^{i\mathbf{K}\cdot\mathbf{L}}$ is independent of the index of the electron which is being moved. This property is guaranteed if the single-particle orbitals ϕ_i that form the Slater determinants in the many-body wave function *all* satisfy the *same* boundary condition $\phi_i(\mathbf{r} + \mathbf{L}) = e^{i\mathbf{k}\cdot\mathbf{L}}\phi(\mathbf{r})$. In other words, the constituent single-particle wave functions all have to correspond to the same k-point of the Brillouin zone of the *simulation* cell. In the case where the simulation cell is a $K \times L \times M$ replica of the primitive cell, the constituent single-particle wave functions have to fall on a (possibly shifted) $K \times L \times M$ Monkhorst-Pack [32] grid.

We are able to compute momentum densities for a dense k-point grid by repeating the VQMC calculation with several shifted sets of LDA wave functions. With our $2 \times 2 \times 2$ simulation cell, ten calculations, each with a different set of wave functions, were required to obtain a $10 \times 10 \times 10$ k-point resolution. At the same time, we can calculate the momentum density due to just the LDA orbitals, with no Jastrow factor.

Figure 1 shows the effect of the quality of the wave function on the correlation correction to the LDA momentum densities $N_{\text{VQMC}}(\mathbf{k}) - N_{\text{LDA}}(\mathbf{k})$ at selected values of $\mathbf{k}$. The wave function only containing the plasmon term u^P yields a clearly incorrect correction to $N_{\text{LDA}}(\mathbf{k})$. In contrast, the 2-parameter form ($u = u^P + \chi^{\text{CD}}$) first used by Fahy, Wang, and Louie [29] and our best 28-parameter show identical (within statistical error) shifts of weight
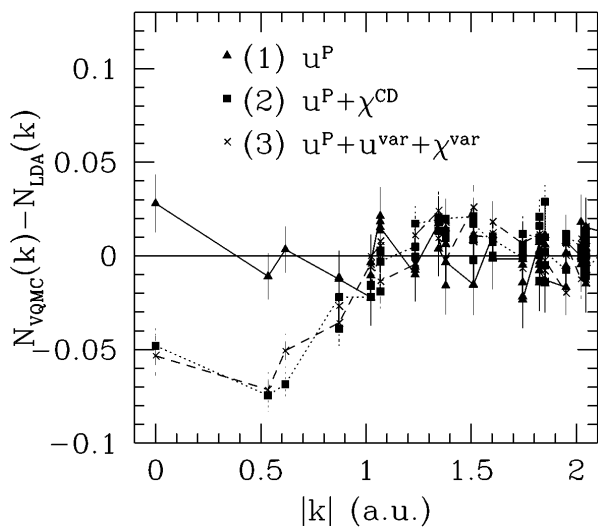
FIG. 1. Momentum density difference between VQMC and LDA calculations with three wave functions in (electrons/primitive cell)/(a.u.)^3 (see text). The graph summarizes data for various directions of **k**. The lines connecting points are a guide to the eye. Expected statistical errors are indicated by vertical bars.
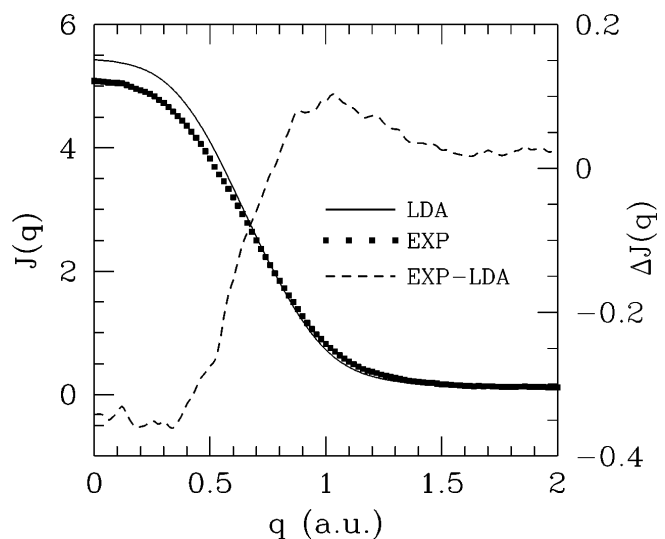

FIG. 2. Comparison between experimental and DFT-LDA valence Compton profiles along the (100) direction in silicon. The left vertical axis gives the scale of the two Compton profiles, and the right vertical axis applies to the difference $\Delta J(q) = J_{\text{EXP}}(q) - J_{\text{LDA}}(q)$.

from low to high momentum values. By analogy to the homogeneous electron gas, we do expect such a weight transfer. The weight transfer is most marked at $|\mathbf{k}| < 1$ a.u., where the momentum density is reduced by approximately 2% of its value at $\mathbf{k} = 0$. The correlation effect is isotropic within the achieved error bars.

In order to compare our calculations to experimental observations, we integrate our momentum densities to obtain Compton profiles. Recall that in the impulse approximation [33,34] the Compton profile is given as a two-dimensional integral of the momentum density,

$$J(\mathbf{q}) = \int d\mathbf{k}' N(\mathbf{k}')\delta(\hat{\mathbf{q}} \cdot \mathbf{k}' - q).$$

In Fig. 2 we plot an experimental valence Compton profile [9] and the results of an *ab initio* DFT-LDA calculation for the valence Compton profile along the (100) direction in silicon, as well as the difference $\Delta J(q)$ between these two curves. The calculation is performed within the pseudopotential approximation and the resulting pseudo-wave-functions are reconstructed to regain oscillations in the core regions as described in [22]. The LDA curve agrees closely with other theoretical predictions [23,24]. Figure 3 shows the correlation correction to the directional profiles in three high-symmetry directions. Correlations beyond the DFT-LDA cause weight to shift from lower to higher momenta. The correction is isotropic within the achieved error bars. The reduction of weight at $\mathbf{k} = 0$ corresponds to approximately 1% of the $\mathbf{k} = 0$ magnitude of the valence Compton profile. We find that correlation corrections are responsible for about 25% of the difference between the best theoretical calculations (Refs. [22–24]) of the valence Compton profile and experiment.

The standard method to include correlation effects beyond the single-particle picture into momentum density and Compton profile calculations has been the Lam-Platzman correction [35] in the LDA. This correction to the momentum density is, in principle, exact in the framework of density functional theory, but is approximate and isotropic in the LDA. We computed the Lam-Platzman correction to silicon Compton profiles within the LDA using diffusion Monte Carlo data for the homogeneous
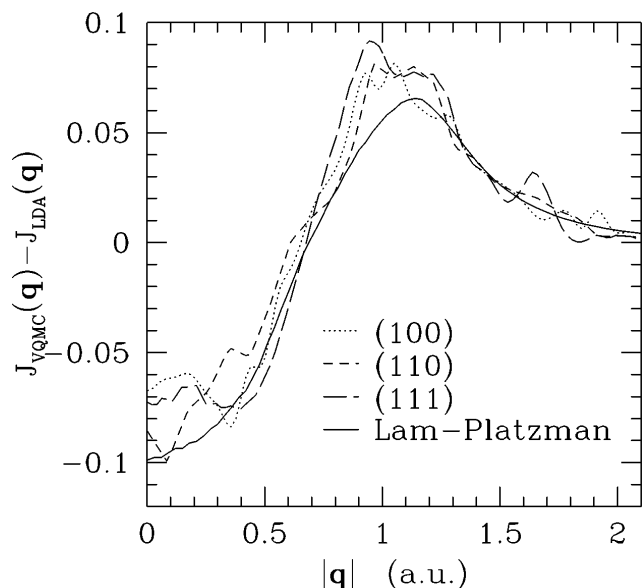

FIG. 3. Correlation correction to the LDA Compton profile of silicon. The standard error associated with the VQMC data is 0.01.

electron gas given by Ortiz and Ballone [36]. The momentum density corrections were then integrated to yield correlation corrections to the Compton profiles. Figure 3 shows the Lam-Platzman correction along with our VQMC results, which may depend on direction. The two computations are in quite good agreement.

In conclusion, we computed, for the first time, the VQMC correlation correction to the valence Compton profile of silicon. We have shown that, although sophisticated variational wave functions are necessary to obtain a good estimate of the ground-state energy of silicon, the correct momentum density is already obtained with the simple 2-parameter variational wave function first used by Fahy, Wang, and Louie [29] for solids. Our results show that valence correlation effects can be ruled out as the dominant source of discrepancy between experimentally observed and calculated Compton profiles of silicon. This indicates that some other nontrivial physics must be present for which the Compton profile acts as a sensitive probe. These effects could include the failure of the impulse approximation, core-core interaction effects, experimental uncertainty, or multiple-scattering corrections.

It is further found that the Lam-Platzman correction predicts this correction accurately for Si. We expect that correlation corrections to momentum densities and Compton profiles of systems whose ground-state properties are well described within the LDA, such as simple metals, will be similarly well described by the Lam-Platzman correction. It remains an interesting open question as to what happens for systems where the LDA is not adequate. Momentum densities in, for example, transition metal oxides could exhibit novel features not captured by the LDA and the Lam-Platzman correction.

[1] B. Williams, *Compton Scattering* (McGraw-Hill, New York, 1976).

[2] J. W. M. Du Mond, Phys. Rev. **33**, 643 (1925).

[3] G. Loupias, J. Petiau, A. Issolah, and M. Schneider, Phys. Status Solidi B **102**, 79 (1980).

[4] Y. Sakurai *et al.,* Rev. Sci. Instrum. **63**, 1190 (1992).

[5] A. Berthold *et al.,* Nucl. Instrum. Methods Phys. Res., Sect. A **317**, 373 (1992).

[6] C. Blaas *et al.,* Phys. Rev. Lett. **75**, 1984 (1995).

[7] Y. Sakurai *et al.,* Phys. Rev. Lett. **74**, 2252 (1995).

[8] K. Hamalainen *et al.,* Phys. Rev. B **54**, 5453 (1996).

[9] Informal Proceedings of the Second International Workshop on Compton Scattering and Fermiology, Tokyo, Japan, 1995 (unpublished).

[10] N. Shiotani *et al.,* J. Phys. Condens. Matter **1**, SA27 (1989).

[11] N. Sakai *et al.,* J. Phys. Soc. Jpn. **58**, 3270 (1989).

[12] W. A. Reed and P. Eisenberger, Phys. Rev. B **6**, 4596 (1972).

[13] W. Schulke, Phys. Status Solidi B **62**, 453 (1974).

[14] P. Pattison and J. R. Schneider, Solid State Commun. **28**, 581 (1978).

[15] P. Pattison, N. K. Hansen, and J. R. Schneider, Chem. Phys. **59**, 231 (1981).

[16] N. K. Hansen, P. Pattison, and J. R. Schneider, Z. Phys. B **66**, 305 (1987).

[17] J. C. Erskine and J. D. McGervey, Phys. Rev. **151**, 615 (1966).

[18] K. Fujiwara and T. Hyodo, J. Phys. Soc. Jpn. **35**, 1133 (1973).

[19] G. Dlubek and W. Brummer, Phys. Status Solidi B **73**, K107 (1976).

[20] A. Seth and D. E. Ellis, J. Phys. C **10**, 181 (1977).

[21] H. Nara, K. Shindo, and T. Kobayashi, J. Phys. Soc. Jpn. **46**, 79 (1979).

[22] P. Delaney, B. Kralik, and S. G. Louie, Phys. Rev. B (to be published).

[23] A. Bansil, 1995 (unpublished).

[24] C. Blaas, 1995 (unpublished).

[25] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).

[26] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[27] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048–5079 (1981).

[28] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566–569 (1980).

[29] S. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. B **42**, 3503 (1990).

[30] A. J. Williamson *et al.,* Phys. Rev. B **53**, 9640 (1996).

[31] S. Fahy, X. W. Wang, and S. G. Louie, Phys. Rev. Lett. **65**, 1478 (1990).

[32] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[33] P. M. Platzman and N. Tzoar, Phys. Rev. **139**, 410 (1965).

[34] P. Eisenberger and P. M. Platzman, Phys. Rev. A **2**, 415 (1970).

[35] L. Lam and P. M. Platzman, Phys. Rev. B **9**, 5122 (1974).

[36] G. Ortiz and P. Ballone, Phys. Rev. B **50**, 1391 (1994).