Ab initio Compton maps of small molecules

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A closed form expression for the evaluation of directional Compton profiles (DCP) from the position space one-electron reduced density matrix expanded in Cartesian Gaussian basis functions is presented. The Compton map, i.e. a two-dimensional contour plot of the DCP function $J(q)$ in a selected plane, is introduced as a convenient method for describing the DCP anisotropy. Symmetry properties of $J(q)$ and its multivaluedness at $|q| = 0$ are discussed. Examples of theoretical Compton maps are given for the hydrogen molecule ion (both ground and excited states), water, ammonia, ethylene and $^1A_1$ methylene molecules in their ground states. Compton maps generated with Hartree–Fock, configuration interaction and density functional theory methods are compared.

1. Introduction

Inelastic scattering of high-frequency photons (X-rays or $\gamma$-rays) by electrons, known as the Compton effect, results in an energy loss of the photons, termed the Compton shift, and the Doppler broadening of the shifted line. Several reviews [1–6] on Compton scattering provide a comprehensive exposition of the subject. In the act of collision, a photon with momentum $k_1$ and energy $\epsilon_1$ is absorbed and another photon with momentum $k_2$ and energy $\epsilon_2$ is emitted, transferring momentum $\mathbf{k} = k_1 - k_2$ and energy $\epsilon = \epsilon_1 - \epsilon_2 = c(|k_1| - |k_2|)$. The angle $\phi$ between $k_1$ and $k_2$ is called the scattering angle. The frequency of the incident radiation is usually so high that the energy transferred to the electron is greater than its binding energy.

Theories of Compton scattering are commonly based on the impulse approximation—the assumption that the momentum exchange between the photon and the electron occurs instantaneously, meaning that the electron does not move during the interaction and then is ejected so quickly that the potential seen by the electron remains the same immediately before and immediately after the collision [6]. This allows the target electron moving in a binding potential to be treated as a free electron with the same momentum. After the knock-out, the electron is explicitly represented by a plane wave. The impulse approximation is adequate only if the energy of the incident ray is many times higher than the electron’s binding energy, i.e. $|k_1| \gg |k|$. This condition implies [7] that in an experimental set-up using monochromatic high-frequency radiation the momentum transfer $k = |\mathbf{k}|$ is effectively fixed by a single parameter—the scattering angle—according to the equation $k = 2k_1 \sin (\phi/2)$.

Measurements of the Doppler broadening of the Compton line provide nearly direct information about the electron momentum distribution in the sample. The fundamental principle of Compton scattering measurements can be understood from a semiclassical description treating the photon as a particle and using equations for the conservation of energy and momentum. An inspection of the momentum conservation diagram [3] leads to the conclusion that, for fixed $k_1$ and $\phi$, the spectrum of the photon energy loss appears as a broad line whose shape is determined by the distribution of electron momenta along the direction of the momentum transfer,

$$
\epsilon = \frac{k^2}{2\mu} + \frac{p \cdot k}{m},
$$

where $\mu$ is the non-relativistic mass of the electron and $p$ is its initial momentum. A detailed derivation [1] of the impulse approximation shows that, for a given $k$, the differential scattering cross-section is proportional to the one-dimensional probability distribution of the projection of the electron momentum $p$ onto $k$,

$$
\frac{d^2\sigma}{d\Omega \, d\epsilon} \propto \int \Pi(p) \, \delta \left( \frac{k}{m} \left( \frac{k}{|k|} - \frac{mc}{|k|} - \frac{k}{2} \right) \right) \, dp,
$$

where $\Pi(p)$ is the electron density in momentum space and $\hat{k}$ is the unit vector along $k$. It is convenient at this step to introduce a vector having the direction $\mathbf{q} = \hat{k}$ and magnitude $q = p \cdot \hat{k}$. The momentum transferred to the electron must equal the momentum lost by the photon, so...
\[ q = \frac{m_e}{k} \frac{k}{2}. \] (3)

Using the new variable \( \mathbf{q} \), termed the scattering vector, Kajser and Smith [8] wrote the probability distribution of equation (2) in the form

\[ J(\mathbf{q}) = \int \int \Pi(p) \delta(p \cdot \hat{q} - q) \, dp. \] (4)

The function \( J(\mathbf{q}) \), called the directional Compton profile (DCP), is a double integral of the momentum density over planes orthogonal to \( \hat{q} \) at a distance \( q = |\mathbf{q}| \) from the origin. In the bulk of the literature, the scattering vector is usually taken to define the \( p_z \) direction in the system’s momentum space, in which case the DCP is written as

\[ J(p_z) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Pi(p) \, dp_x \, dp_y. \] (5)

The DCP function \( J(\mathbf{q}) \) contains complete information about the momentum distribution in the system. Within the impulse approximation, \( J(\mathbf{q}) \) predicts the shape of the Compton line measured along \( \hat{q} \). It has the dimension of inverse momentum, i.e. \( p_0^{-1} \) using atomic units of momentum (\( p_0 = h/a_0 \), where \( a_0 \) is the Bohr radius) and is normalized as

\[ \int_{-\infty}^{\infty} J(q \hat{q}) \, dq = N, \] (6)

where \( N \) is the number of electrons. Averaging \( J(q \hat{q}) \) over all directions yields the isotropic Compton profile \( J(q) \), which is just a one-dimensional function.

The relationship between the one-dimensional probability distribution \( J(p_z) \) defined by equation (5) and the three-dimensional distribution \( \Pi(p_x, p_y, p_z) \) can be emphasized by pointing to the seemingly missing link, the two-dimensional function

\[ P(p_z, p_z) = \int \Pi(p) \, dp_z. \] (7)

In fact, the probability distribution \( P(p_z, p_z) \) was introduced many years ago by Coulson [9] and used to visualize electron momentum distributions in planar molecules.

As implied in the foregoing discussion, the observed Compton profile is comprised of contributions from all electrons of the system. Considering that momentum distributions of core electrons approach spherical symmetry, one would expect that any directional anisotropy of \( J(q) \) is caused primarily by valence electrons. The difference between DCPs along two selected directions \( \hat{q}_1 \) and \( \hat{q}_2 \) (usually taken along directions of symmetry),

\[ \Delta J(q) = J(q \hat{q}_1) - J(q \hat{q}_2), \] (8)

is a convenient definition of the Compton profile anisotropy in solids. The recent measurement of \( \Delta J(q) \) in molecular crystals of ice [10] has been a spectacular achievement.

A peculiar property of the DCP function \( J(\mathbf{q}) \) is that its value at \( |\mathbf{q}| = 0 \) depends on the orientation of the integration plane. This dependence is conveniently visualized by the \( J(0 \hat{q}) \) surface of Janis et al. [11], i.e. a collection of points defined by vectors centred at the origin, whose direction and length are given by \( \mathbf{q} \) and \( J(\mathbf{q}) \) at \( |\mathbf{q}| = 0 \), respectively. Deviations of the \( J(0 \hat{q}) \) surface from a perfect sphere characterize the zero-momentum Compton profile anisotropy.

In the present paper we introduce another natural representation of the DCP anisotropy by means of the Compton map. A Compton map is a two-dimensional contour plot of a section through the three-dimensional distribution \( J(\mathbf{q}) \). Note the analogy with momentum density maps and contours of constant probability \( P(p_x, p_y) \). To our knowledge, maps of the Compton profile function have not been discussed in the literature. We derive a closed form expression for \( J(\mathbf{q}) \) and describe an algorithm for the evaluation of Compton maps from the position space one-electron reduced density matrix.

Although a large amount of directional Compton scattering data has been collected for ionic crystals and metals, observation of directional profiles for free molecules remains elusive in view of experimental constraints. Meanwhile, theoretical Compton maps may be useful in discussing the structure of momentum densities and the character of chemical bonds, as we demonstrate here by the examples of small molecules.

Realizing that the Compton profile anisotropy is rather sensitive to the quality of the approximate wave function, we also compare Compton maps generated with various \textit{ab initio} and density functional theory methods.

2. Evaluation of directional Compton profiles

Several methods are available for the evaluation of directional and isotropic Compton profiles [8, 12–15]. Calculations on crystalline systems are routinely performed at the Hartree–Fock (HF) level with a plane wave basis, in which case the expressions for \( \Pi(p) \) and \( J(\mathbf{q}) \) are rather straightforward. Molecular calculations, however, often employ post-Hartree–Fock techniques and almost invariably rely on localized basis functions in position space. Accordingly, the general procedure for obtaining momentum distributions involves a non-trivial Fourier–Dirac transformation of the one-electron reduced density matrix \( \rho(\mathbf{r} \mathbf{r'}) \) derived from a position space wave function,
\[ II(\mathbf{p}) = II(\mathbf{p}\mathbf{\bar{p}}) \]
\[ = \frac{1}{(2\pi)^{3\ell}} \int \exp(-i\mathbf{p} \cdot \mathbf{r}/h)\rho(\mathbf{r}\mathbf{r}') \times \exp(+i\mathbf{p} \cdot \mathbf{r}'/h) \, d\mathbf{r} \, d\mathbf{r}' . \]  

One proceeds by inserting into equation (4) the above expression for the momentum density and the Fourier integral representation for the one-dimensional \( \delta \) function,

\[ \delta(\mathbf{p} \cdot \mathbf{q} - q) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp[i(\mathbf{p} \cdot \mathbf{q} - q)] \, dt . \]  

After some manipulation this gives

\[ J(\mathbf{q}) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-iqs/h) ds \int \rho(\mathbf{r}\mathbf{r} - s) \, d\mathbf{r} . \]  

The reduced density matrix can always be expanded in a basis of one-electron functions, such as Slater-type or Gaussian-type orbitals (GTOs),

\[ \rho(\mathbf{r}\mathbf{r}') = \sum_{i,j} P_{ij} f_i(\mathbf{r}) f_j^*(\mathbf{r}') , \]

where \( P_{ij} \) is an element of the discrete representation \( \mathbf{P} \) of \( \rho(\mathbf{r}\mathbf{r}') \). Thus the Fourier–Dirac transformation of \( \rho(\mathbf{r}\mathbf{r}') \) reduces to the calculation of the Fourier transforms of individual basis functions [13].

Only a few published algorithms for the evaluation of Compton profiles with localized basis functions avoid numerical integration in equation (12) entirely. We are aware of two such approaches for GTOs: the method of Rérat and Lichanot [14] for the calculation of DCPs from HF and configuration interaction (CI) wave functions, which uses recursive formulas for the Fourier transforms of primitive Gaussians, and the algorithm of Saenz et al. [15] for the evaluation of spherically averaged Compton profiles and reciprocal form factors.

Our procedure, which stresses use of the density matrix rather than individual configurations in the CI expansion, is as follows. In the first step, the density matrix from a molecular wave function calculation is converted by a suitable linear transformation to the basis of unnormalized primitive Cartesian GTOs,

\[ \rho(\mathbf{r}\mathbf{r}') = \sum_{A,B} P_{AB} g_A(\mathbf{r} - \mathbf{R}_A) g_B^*(\mathbf{r}' - \mathbf{R}_B) , \]

where \( P_{AB} \) is a matrix element of the discrete representation of \( \rho(\mathbf{r}\mathbf{r}') \) in the GTO basis, and the summation is over all \( AB \) pairs of basis functions

\[ g_A(\mathbf{r} - \mathbf{R}_A) = (x - X_A)^{L_A}(y - Y_A)^{M_A}(z - Z_A)^{N_A} \times \exp\left( -\alpha_A |\mathbf{r} - \mathbf{R}_A|^2 \right) , \]  

\[ g_B(\mathbf{r} - \mathbf{R}_B) = (x - X_B)^{L_B}(y - Y_B)^{M_B}(z - Z_B)^{N_B} \times \exp\left( -\alpha_B |\mathbf{r} - \mathbf{R}_B|^2 \right) , \]  

centred at \( \mathbf{R}_A = (X_A, Y_A, Z_A) \) and \( \mathbf{R}_B = (X_B, Y_B, Z_B) \), respectively. The normalization factors of GTOs can be incorporated into the matrix \( \mathbf{P} \). The DCP can now be obtained by substituting equation (14) into equation (12). Assuming that the basis functions are real and that all quantities are in atomic units \( (h = 1, a_0 = 1) \), we have

\[ J(\mathbf{q}) = \frac{1}{2\pi} \sum_{A,B} P_{AB} G_{AB}(\mathbf{q}) , \]

where

\[ G_{AB}(\mathbf{q}) = \int_{-\infty}^{\infty} \exp(-iqs/h) ds \times \int g_A(\mathbf{r} - \mathbf{R}_A) g_B(\mathbf{r} - \mathbf{R}_B - s) \, d\mathbf{r} . \]

The overlap integral in equation (18) is evaluated by substitution of equations (15) and (16) and repeated use of the binomial expansion formula, as described by Saenz et al. [15]. The result is

\[ J(\mathbf{q}) = \frac{1}{2\pi} \sum_{A,B} P_{AB} \left( \frac{\pi}{\alpha_A + \alpha_B} \right)^{3/2} \times \sum_{L_A=0}^{L_a} \sum_{L_B=0}^{L_b} \left( \frac{L_A}{l_A} \frac{L_B}{l_B} \right) (l_A + l_B - 1)!! \times \left( \frac{\alpha_A}{\alpha_A + \alpha_B} \right)^{L_A - l_A} \left( \frac{\alpha_B}{\alpha_A + \alpha_B} \right)^{L_B - l_B} \times \sum_{m_A=0}^{L_A} \sum_{m_B=0}^{L_B} \left( \frac{M_A}{m_A} \right) (M_B/m_B) (m_A + m_B - 1)!! \times \left( \frac{\alpha_A + \alpha_B}{\alpha_A + \alpha_B} \right)^{M_A + M_B - (m_A + m_B)/2} \times \sum_{n_A=0}^{N_A} \sum_{n_B=0}^{N_B} \left( \frac{N_A}{n_A} \frac{N_B}{n_B} \right) (n_A + n_B - 1)!! \times \left( \frac{\alpha_A}{\alpha_A + \alpha_B} \right)^{N_A - n_A} \left( \frac{\alpha_B}{\alpha_A + \alpha_B} \right)^{N_B - n_B} \times F(L, M, N, c, \beta; q) , \]
where \( L = L_A + L_B - I_A - I_B, M = M_A + M_B - m_A - m_B, N = N_A + N_B - n_A - n_B, \beta = \alpha_A \alpha_B / (\alpha_A + \alpha_B) \) and the vector \( c = R_A - R_B = (c_x, c_y, c_z) \) parametrizes the function

\[
F(L, M, N, c, \beta; q) = \int_{-\infty}^{\infty} \exp(-i q s) \exp(-\beta|s|^2) \times (c_x - s_x)^L(c_y - s_y)^M(c_z - s_z)^N \, ds.
\]

(20)

The Fourier transform of the Cartesian Gaussian in equation (20) is a linear combination of Gaussians multiplied by Hermite polynomials [8]. Rather than following the general formalism, we shall obtain the same result in a more explicit manner. First, using the binomial expansion and substituting \( s_x = s_q \), etc., we write

\[
F(L, M, N, c, \beta; q) = \sum_{l=0}^{L} \sum_{m=0}^{M} \sum_{n=0}^{N} \binom{L}{l} \binom{M}{m} \binom{N}{n} (-1)^{l+m+n} \times c_x^{L-l} c_y^{M-m} c_z^{N-n} s_x^{l} s_y^{m} s_z^{n} \times \int_{-\infty}^{\infty} \exp(-i q s - \beta|c - s|^2) \, ds.
\]

(21)

where \((\hat{q}_x, \hat{q}_y, \hat{q}_z)\) are the components of the unit vector \( \hat{q} \). In order to evaluate the integral

\[
I = \int_{-\infty}^{\infty} s^{l+m+n} \exp(-i q s - \beta|c - s|^2) \, ds,
\]

we rearrange the exponential expression to obtain the full square of the \( s \) term,

\[
-\beta|s|^2 = -\beta \left[ s - \left( \frac{q \cdot c}{2\beta} \right) \right]^2
\]

\[
-\beta \left[ \frac{q^2}{4\beta^2} - (\hat{q} \cdot c)^2 \right] - i q \cdot c.
\]

(23)

Now let

\[
\gamma = \hat{q} \cdot c - \frac{i q \cdot c}{2\beta}
\]

(24)

be a new complex variable. By changing the integration variable in \( I \) from real to complex according to \( \xi = s - \gamma \), \( d\xi = ds \), and using the shorthand \( K = l+m+n \), we obtain

\[
I = \exp\left\{ -\beta \left[ \frac{q^2}{4\beta^2} - (\hat{q} \cdot c)^2 \right] \right\} \exp(-i q \cdot c)
\]

\[
\times \int_{-\infty}^{\infty} (\xi + \gamma)^K \exp(-\beta\xi^2) \, d\xi.
\]

(25)

The binomial expansion followed by contour integration yields

\[
\int_{-\infty}^{\infty} (\xi + \gamma)^K \exp(-\beta\xi^2) \, d\xi
\]

\[
= \sum_{k=0}^{K} \binom{K}{k} \gamma^{K-k} \int_{-\infty}^{\infty} \exp(-\beta\xi^2) \, d\xi
\]

\[
= \sum_{k=0}^{K} \binom{K}{k} \gamma^{k} \left( \frac{K}{2\beta} \right)^{K/2} \left( \frac{\pi}{\beta} \right)^{1/2}.
\]

(26)

The complex variable \( \gamma \) can be represented as \( \gamma = w \exp(-i\theta) \), where

\[
w = \left( \frac{(q \cdot c)^2}{(2\beta)} \right)^{1/2},
\]

\[
\theta = \cos^{-1} \left( \frac{q \cdot c}{w} \right), \quad 0 \leq \theta \leq \pi.
\]

(27)

Then

\[
I = \exp\left\{ -\beta \left[ \frac{q^2}{4\beta^2} - (\hat{q} \cdot c)^2 \right] \right\} \times \sum_{k=0}^{K} \binom{K}{k} \left( \frac{k-1}{2\beta} \right)^{K-k} \exp\left\{ -i(q \cdot c + (K-k)\theta) \right\}.
\]

(29)

Since the basis functions are assumed to be real, the matrix representation of \( \rho(r|r') \) in equation (17) is symmetric, i.e. \( P_{AB} = P_{BA} \), while \( G'_{AB} = G_{BA} \) (see equation (18)). Therefore,

\[
P_{AB}G_{AB}(q) + P_{BA}G_{BA}(q) = P_{AB}G_{AB}(q) + G_{AB}(q)
\]

\[
= 2P_{AB} \Re[G_{AB}(q)].
\]

(30)

Thus, \( J(q) \) is real, so we need only the real part of equation (29). Substitution of \( \Re[I] \) into equation (21) yields

\[
F(L, M, N, c, \beta; q)
\]

\[
= \left( \frac{\pi}{\beta} \right)^{1/2} \exp\left\{ -\beta \left[ \frac{q^2}{4\beta^2} - (\hat{q} \cdot c)^2 \right] \right\} \times \sum_{l=0}^{L} \sum_{m=0}^{M} \sum_{n=0}^{N} \sum_{k=0}^{l+m+n} \binom{L}{l} \binom{M}{m} \binom{N}{n} \binom{k-1}{2\beta}^{l+m+n} \times \cos[q \cdot c + (l+m+n-k)\theta].
\]

(31)

where \( w \) and \( \theta \) are defined by equations (27) and (28). The combination of equations (19) and (31) is the desired closed form expression for the DCP function.
3. Properties of Compton maps

Elementary properties of the function \( J(\mathbf{q}) \) were reviewed in the introduction. In this section we shall discuss the features that are relevant to the structure of Compton maps, in particular the symmetry of \( J(\mathbf{q}) \) and its behaviour at the origin of momentum space.

3.1. Symmetry properties of \( J(\mathbf{q}) \)

In the absence of degenerate open shells, the exact electron charge density \( \rho(\mathbf{r}) \) of a molecule belongs to the same point group \( G^0 \) as the nuclear configuration and forms a basis for the totally symmetric irreducible representation of that group. The charge density derived from an approximate wave function will have this property only if the basis set is closed under the symmetry operations of \( G^0 \) and the total symmetry is not broken by some artefact.

The symmetry of the exact electron momentum density \( \Pi(\mathbf{p}) \) of the fixed nuclei approximation is characterized by the presence of inversion, which is implied by the requirement that the entire electronic system be at rest. Although the momentum distribution derived from an approximate wave function does not necessarily have this property, in the case of a real wave function inversion symmetry in momentum space is guaranteed [16–20]. Defranceschi and Berthier [18] formally showed that if the electron density \( \rho(\mathbf{r}) \) is totally symmetric under a \( G^0 \) point group and the wave function expressed in position space is pure real or pure imaginary, then the transformation to momentum space introduces an inversion centre \( i \) and leads to an electron momentum distribution \( \Pi(\mathbf{p}) \) totally symmetric under the \( G^0 \times i \) point group. Thus, the point group \( G \) of momentum density is formed as the semidirect product of the groups \( G^0 \) and \( C_i \). Clearly, if \( G^0 \) already contains \( i \), then \( G = G^0 \).

Within the impulse approximation, the function \( J(\mathbf{q}) \) is totally symmetric under the same point group \( G \) as the momentum distribution, as will be now shown. Let \( \mathcal{G} \) be a symmetry operator of the group \( G \). Because \( \mathcal{G} \) leaves the scalar product of two vectors unchanged, we have from \( \mathbf{q} \cdot \mathbf{p} = (\mathcal{G}\mathbf{q}) \cdot (\mathcal{G}\mathbf{p}) \) the identity \( (\mathcal{G}^{-1}\mathbf{q}) \cdot \mathbf{p} = \mathbf{q} \cdot (\mathcal{G}\mathbf{p}) \). Therefore,

\[
\mathcal{G}J(\mathbf{q}) = J(\mathcal{G}^{-1}\mathbf{q}) = \int \Pi(\mathbf{p}) \delta(\mathbf{p} \cdot \mathbf{q} - q) \, d\mathbf{p} = \int \Pi(\mathbf{p}) \delta((\mathcal{G}\mathbf{p}) \cdot \mathbf{q} - q) \, d\mathbf{p}.
\]

(32)

Let us now change the integration variable to \( \mathbf{p}' = \mathcal{G}\mathbf{p} \). The symmetry operation \( \mathcal{G} \) leaves the volume element \( d\mathbf{p} \) unchanged, so sequence (32) is continued as

\[
\mathcal{G}J(\mathbf{q}) = \int \Pi(\mathcal{G}^{-1}\mathbf{p}') \delta(\mathbf{p}' \cdot \mathbf{q} - q) \, d\mathbf{p}' = \int \Pi(\mathbf{p}') \delta(\mathbf{p}' \cdot \mathbf{q} - q) \, d\mathbf{p}' = J(\mathbf{q}),
\]

(33)

because, by assumption, \( \Pi(\mathbf{p}') = \Pi(\mathbf{p}) \). Since \( J(\mathbf{q}) \) is invariant under all symmetry operations of \( G \), and only those operations, it belongs to the totally symmetric irreducible representation of the same group.

A Compton map is a two-dimensional object and, hence, may partly retain the symmetry of \( J(\mathbf{q}) \). For instance, a Compton map passing through the origin of momentum space always has inversion symmetry. High-precision measurements reveal a specific asymmetry in the intensities of the positive and negative branches of the Compton line as well as a shift of its peak from \( q = 0 \), collectively known as the Compton defect [21]. The Compton defect is caused by breakdown of the impulse approximation and destroys the simple relationship between the symmetries of \( \Pi(\mathbf{p}) \) and experimental \( J(\mathbf{q}) \).

3.2. Multivaluedness of \( J(\mathbf{q}) \) at zero momentum

As stated by equation (4), the DCP function \( J(\mathbf{q}) \) is an integral of momentum density over the plane perpendicular to \( \mathbf{q} \) at the distance \( q \) from the origin. The integration plane and, hence, the value of \( J(\mathbf{q}) \) are uniquely defined at any point \( \mathbf{q} \), provided that \( |\mathbf{q}| > 0 \). However, there are infinitely many planes distinguishable by their orientation such that \( \mathbf{q} = 0 \). Thus, the origin of momentum space is a special point at which \( J(\mathbf{q}) \) is not analytic. As mentioned above, the \( J(\mathbf{0}) \) surface reflects this fact by deviations from the spherical shape. On Compton maps, the multivaluedness of \( J(\mathbf{q}) \) at zero momentum is manifested by the intersection of distinct contours at the point \( \mathbf{q} = \mathbf{0} \). These and more specific features of molecular Compton maps are illustrated by the following examples.

4. Computational details

The computer program for the evaluation of \( J(\mathbf{q}) \) has at its core the finite series expansion in powers of \( \hat{q}_x, \hat{q}_y, \hat{q}_z \) and \( w \).

\[
J(\mathbf{q}) = \sum_{A B} P_{AB} \exp \left\{ -\beta^2 (q_x^2 + q_y^2 + q_z^2 - (\mathbf{q} \cdot \mathbf{c})^2) \right\} \times \sum_{l m n} f_{l m n k} q_x^l q_y^m q_z^n w^{l+m+n-k} \cos |\mathbf{q} \cdot \mathbf{c} + (l + m + n - k)\theta|,
\]

(34)

where \( \mathbf{c} \) and \( \theta \) are defined by equations (27) and (28), while coefficients \( f_{l m n k} \) incorporate \( \mathbf{q} \) and \( w \)-independent parameters of equations (19) and (31). The values of \( l, m, n, k \) are subject to specific restrictions. Each coeffi-
cient $f_{lmnk}$ (non-zero only for an admissible set $l,m,n,k$) depends solely on a given pair of primitive Gaussians. Therefore, it has the same value for all grid points $\mathbf{q} = (q_x, q_y, q_z)$ and is computed just once for each distinct pair of GTOs. The evaluation of the entire set of coefficients $f_{lmnk}$ for a given pair of basis functions is followed by the scan over grid points which returns the value of $P_{AB}G_{A\beta}(\mathbf{q})$ (see equation (17)).

Formula (34) requires a discrete $\mathbf{P}$ matrix corresponding to the one-electron density matrix $\rho(\mathbf{r}|\mathbf{r'})$. This is very convenient in molecular calculations where $\mathbf{P}$ is part of routine output. Given a one-electron basis, the dimension of $\mathbf{P}$ is the same regardless of the complexity of the wave function. The symmetry of the $\mathbf{P}$ matrix was used to halve the number of cycles over primitive GTOs.

$\mathbf{P}$ matrices were obtained from self-consistent field (SCF) and configuration interaction (CI) wave functions using the MELD [22] series of programs. All calculations were carried out using Dunning's aug-cc-pVTZ (augmented correlation consistent polarized valence triple-zeta) basis set [23], i.e. $(10s5p2d1f)/[4s3p2d1f]$ contractions for first-row atoms augmented with diffuse $(1s1p1d1f)$ functions and $(5s2p1d)/[3s2p1d]$ contractions augmented with diffuse $(1s1p1d)$ functions for hydrogen. This basis has 5 component $d$- and 7 component $f$-functions.

5. Results and discussion

5.1. Hydrogen molecule ion

The $H_2^+$ ion has been historically important in understanding the nature of the chemical bond viewed both in position and momentum space [24–26]. The unusual topography of the momentum density in $H_2^+$ is of particular interest, as it is directly related to the structure of Compton maps. Simas et al. [27] showed that in momentum distributions of one-electron homonuclear diatomics there exists an infinite sequence of nodal surfaces (but not planes, unless a minimum basis description is adopted). These surfaces intersect with the $p_z$ axis (the direction parallel to the internuclear axis). The nodal surfaces of $\Pi(\mathbf{p})$ in the ground ($1\sigma_g$) state are seen in figure 1(a), and their intersections with the $p_z$ axis are precisely matched by minima of $J(\mathbf{q})$ occurring along the axial direction (figure 1(b)). Both distributions $\Pi(\mathbf{p})$ and $J(\mathbf{q})$ were computed at the ground state equilibrium internuclear distance $r_e = 1.9972\, a_0$ [28] and have the symmetry of the molecule, i.e. $D_{\infty h}$. The behaviour of $J(\mathbf{q})$ depends fundamentally on the direction of the scattering vector $\mathbf{q}$. In the directions perpendicular to the internuclear axis, $J(\mathbf{q})$ decays monotonically from the origin whereas along the axis it oscillates. Kajiser and Smith [29] pointed out that $J(\mathbf{q})$ will vanish if and only if there exist nodal planes in $\Pi(\mathbf{p})$. Since the nodal surfaces of $\Pi(\mathbf{p})$ are not planes, the function $J(\mathbf{q})$ does not vanish even at its minima along the $p_z$ axis. As noted by Coulson [25], the electron momentum in the bonding state of $H_2^+$ is more likely to be directed perpendicular to rather than along the bond. This trend, generalized in the form of the bond directional principle [1, 30], is revealed by horizontal elongation of closed contours in both plots.

The momentum density and the corresponding Compton map for the first excited ($1\sigma_u$) state at the ground state equilibrium distance appear in figures 1(c) and (d). As in the case of the ground state, periodic nodal surfaces in $\Pi(\mathbf{p})$ result in oscillations of $J(\mathbf{q})$ along the direction of the internuclear axis.

From figures 1(b) and (d) one can infer that the DCP anisotropy $\Delta J(q) = J_x(q) - J_z(q)$ at small $q$ is positive for the $1\sigma_g$ state and negative for the $1\sigma_u$ state. The sign of $\Delta J(0)$ for diatomic molecules is thought to be related to the type of charge redistribution upon combining the atoms and, therefore, may give an idea about the bonding or anti-bonding character of the chemical bond. However, it is not a rigorous criterion and many exceptions are known [30].
5.2. Water

Compton profiles of only a few molecular compounds have been investigated, whether experimentally or theoretically. Of these, water is a relatively frequent object of study. A number of experimental isotropic Compton profiles for water [31, 32] have long been available for comparison with theory [33–35].

The symmetry group of the H$_2$O molecule, $C_2v$, does not include inversion. Transformation to momentum space introduces inversion in momentum distributions and leads to the D$_{2h}$ symmetry. The presence of the new symmetry property of $J(q)$ is seen on the Compton maps for H$_2$O in figures 2 (a) and (b). These were computed at the best available ground state equilibrium geometry of the molecule: $\langle OH\rangle = 1.8101$ $a_0$, $\theta$(HOH) = 104.54° [36]. The density matrix was obtained from the CI wave function that includes single and double excitations (SD) relative to the Hartree–Fock reference configuration. With the aug-cc-pVTZ basis set, this CI expansion includes 25 093 spin- and symmetry-adapted configurations. Unlike the Compton maps for H$_2^+$, the maps for H$_2$O do not show oscillations of $J(q)$ in any direction, because molecular systems with more than one electron cannot have nodal surfaces in their ground state momentum distributions [27]. In fact, $J(q)$ becomes almost isotropic at $|q| > 0.75 p_0$, because the outer regions of a Compton map reflect contributions from core electrons whose momenta exhibit highly isotropic directional distributions. Here, and in further examples, we shall see that the characteristic pattern of a Compton map (the ‘signature’) appears near its centre, i.e. at the lowest values of electron momentum projections. This observation agrees with the common assumption that the individual properties of molecules are determined almost exclusively by the slower valence electrons.

It is well known that an improvement of the SCF wave function by admixing excited configurations has the effect of shifting the average electron momentum to higher values. The influence of electron correlation on theoretical isotropic Compton profiles of water and basis set effects on the molecule’s DCPs have been specifically addressed in the earlier literature [37, 38]. In figures 2 (c) and (d) we show the contribution of excited configurations to $J(q)$ defined as

$$\delta J_{CI}(q) = J_{CI}(q) - J_{SCF}(q) .$$  (35)

The contour plots of $\delta J_{CI}(q)$ are drawn here for two mutually perpendicular planes intersecting along the $C_2$ symmetry axis. While $J_{CI}(q) < J_{SCF}(q)$ in the molecular plane from $q = 0.3 p_0$ to about $q = 1.5 p_0$, values of $J_{CI}(q)$ at the very smallest $q$ are actually slightly greater than $J_{SCF}(q)$. The largest absolute difference $|\delta J_{CI}| = 0.025 p_0^{-1}$ is attained near $q = 0.75 p_0$ in the molecular plane and constitutes approximately 0.6% of $J(0)$ in the $q_y$ direction. Overall, the value of $\langle q^2 \rangle$ increases from $151.912 p_0^2$ for the SCF wave function to $152.424 p_0^2$ for the CI expansion. For comparison, the exact value of $\langle q^2 \rangle$ derived from the virial theorem is $152.876 p_0^2$ [39].

5.3. Ammonia

The NH$_3$ molecule is isoelectronic with H$_2$O but belongs to a different point group. The C$_{3v}$ symmetry of the electron density of NH$_3$ in position space becomes D$_{3d}$ symmetry in momentum space. Experimental isotropic Compton profiles of ammonia have been observed in studies of the Compton defect [40, 41], and a CI calculation of isotropic $J(q)$ has been reported [35]. We computed Compton maps of ammonia at the equilibrium geometry [42]: $\langle NH \rangle = 1.9099$ $a_0$, and $\theta$(out-of-plane angle) = 22.19°. The wave function (the full SDCI expansion with a single reference HF configuration) includes 77 106 configuration state functions.
Detailed calculations show an increase of the D₃ symmetry plane. As in the case of H₂O, bond, the two N–H bonds stretching outside the symmetrical plane of momentum space. In panels (a), (c) and (d), the lowest contour level is at 2.4ₚ₀⁻¹; the increment is 0.2ₚ₀⁻¹. In panel (b), line style and arrow conventions are as in figures 2(c) and (d); successive contours follow the absolute values (from the nodal contour) 0.010, 0.014, 0.020.

The Compton map in a symmetry plane containing the C₃ axis (see figure 3(a)) is not dissimilar to the in-plane map of H₂O, but the inner contours are now distorted by unbalanced contributions from the in-plane N–H bond, the two N–H bonds stretching outside the symmetry plane. As in the case of H₂O, J(q) becomes nearly isotropic at |q| > 0.75ₚ₀.

Figure 3(b) depicts an outward shift of the distribution J(q) caused by the transition from SCF to SDCI. Detailed calculations show an increase of ⟨p²⟩ from 112.275 to 112.762ₚ₀² (the exact value is 113.126ₚ₀² [43]).

The Compton map in figure 3(a) does not reveal the D₃ₙ symmetry of the DCP function. In order to demonstrate the true symmetry of J(q), we computed additional Compton maps in two planes perpendicular to the C₃ symmetry axis (see figures 3(c) and (d)). One of these planes is 0.05ₚ₀ above and the other 0.05ₚ₀ below the origin of momentum space. The combination of figures 3(c) and (d) illustrates the presence of an inversion centre and three perpendicular C₃ axes contained in the D₃ₙ point group.

5.4. Ethylene

Ethylene (C₂H₄) is the simplest molecule with π carbon–carbon bonding. The symmetry group of ethylene, D₂ₙ, already contains inversion, so the DCP function in the impulse approximation also belongs to the D₂ₙ group. Isotropic Compton profiles of ethylene have been observed experimentally [44, 45]. Detailed calculations of isotropic and directional Compton profiles of ethylene as well as a critical assessment of the earlier results have been reported by Tripathi et al. [46]. Our calculations were performed at the best estimate of the ground state equilibrium geometry of the molecule [47], i.e. r(CC) = 2.5147ₚ₀, r(CH) = 2.0426ₚ₀ and θ(CCH) = 121.44°. Compton maps shown in figures 4(a) and (b) were obtained from the multireference (MR) CI expansion with the 2e⁻/72 orb. (b₃ₓ,b₁ₓ) CASSCF reference state. The reference wave function consists of two configurations, and the entire MRSDCI expansion includes 263 246 configurations.

On the in-plane Compton map of C₂H₄ (figure 4(a)) there exists an X-shaped pattern which can be related to the number and direction of interatomic bonds. Returning to the Compton maps of H₂O and NH₃, we see that their patterns similarly reveal the presence of two and three bonds, respectively. At the same time, distortions of the spherical symmetry of J(q) in ethylene persist through higher momenta than in H₂O and NH₃ molecules. A plausible explanation is that in C₂H₄ there are 12 valence electrons responsible for the anisotropy of J(q) as opposed to only 8 valence electrons in H₂O and NH₃.

Figures 4(c) and (d) show net correlation improvements of J(q) over the SCF result. Consistent with the general trend, δJ_{CI}(q) is negative for small q in all directions. The value of ⟨p²⟩ computed with the MRCI wave function is 156.586ₚ₀² compared with 155.882ₚ₀² for the SCF (the estimated exact value is 157.175ₚ₀² [48]).

5.5. Singlet methylene

No experimental or theoretical Compton profiles of methylene have been reported in the literature. The geometry of ¹A₁ CH₂ adopted here is the optimum geometry of Comeau et al. [49] obtained with a high-quality MRCI wave function: r(CH) = 2.0999ₚ₀ and θ(CCH) = 101.95°. A reasonable description of the ¹A₁ state of methylene requires at least two configurations: ¹a₁²2a₁²1b₁²3a₁² (the SCF determinant) and the low-lying ¹a₁²2a₁²1b₁²1b₁² excited configuration. The density matrix was generated from an MRSDCI wave function (92 117 configuration state functions). The reference wave function was obtained by distributing the 8 electrons of the molecule among the 5 lowest orbitals taken (without re-optimization) from a 2 e⁻/72 orb. (3a₁,1b₁) CASSCF calculation.
In-plane and out-of-plane Compton maps of CH$_2$ are shown in figures 5(a) and (b). The in-plane map is very similar to that of the water molecule, which is not unexpected given the close geometry. However, the out-of-plane map of CH$_2$ is qualitatively different from the corresponding map of H$_2$O, because the out-of-plane $p$-orbital in CH$_2$ is nominally vacant whereas in H$_2$O it is doubly occupied. The essential difference in the electronic structure of the two molecules results in dissimilar out-of-plane momentum distributions.

An improvement of the wave function from SCF to MRSDCI increases the probability of higher electron momentum vectors than the wave function for the CI expansion. The exact value is placed at 78.260 $p_0^1$. The in-plane map is very similar to that of the water molecule, because the out-of-plane $p$-orbital in CH$_2$ is nominally vacant whereas in H$_2$O it is doubly occupied. The essential difference in the electronic structure of the two molecules results in dissimilar out-of-plane momentum distributions.

5.6. Compton maps of methylene from DFT

There has been a sustained interest in applying density functional theory (DFT) to calculations of momentum distributions and Compton profiles [51–54]. The most natural approach is based on the Kohn–Sham (KS) variational calculation of the charge density in terms of KS orbitals, $\rho(r) = \sum_j n_j |\phi_j^{KS}(r)|^2$, followed by the Fourier transformation of $\phi_j^{KS}(r)$,

$$II(p) = \frac{1}{(8\pi)^3} \sum_j n_j \int [\exp(-ip \cdot r)|\phi_j^{KS}(r)|^2] dr^2, \quad (36)$$

where $n_j$ are orbital occupation numbers. This, of course, is not the same as the Fourier transformation of $\rho(r)$ which would produce the so-called form factor. Two considerations are crucial for an assessment of this method. While exact DFT yields exact energies and exact charge densities, most approximations to the exact density functional focus on getting accurate energies with no attention to the accuracy of the electron density. Functionals devised in this way are very successful in predicting energies and molecular geometries, but the electron densities they generate may be defective. Furthermore, the Kohn–Sham formalism is based on the concept of a non-interacting reference state and,
momentum space. The patterns of \( \bar{\rho}(\mathbf{r}) \) and Compton peak values (in \( p_0^2 \)) for the ground state of \( ^1A_1 \)CH\(_2\) (standard molecular orientation).

<table>
<thead>
<tr>
<th>Method</th>
<th>( \langle p^2 \rangle )</th>
<th>( J_z(0) )</th>
<th>( J_z(0) )</th>
<th>( J_\perp(0) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCF(^{a})</td>
<td>77.669</td>
<td>4.685</td>
<td>3.813</td>
<td>3.469</td>
</tr>
<tr>
<td>BLYP(^{a})</td>
<td>77.807</td>
<td>4.746</td>
<td>3.845</td>
<td>3.455</td>
</tr>
<tr>
<td>B3LYP(^{a})</td>
<td>77.739</td>
<td>4.722</td>
<td>3.830</td>
<td>3.454</td>
</tr>
<tr>
<td>MRSDCI(^{a,b})</td>
<td>77.981</td>
<td>4.596</td>
<td>3.769</td>
<td>3.468</td>
</tr>
<tr>
<td>Exact(^{c})</td>
<td>78.260</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Basis set: aug-cc-pVTZ.
\(^{b}\) 92117 configuration state functions.
\(^{c}\) [50].

hence, produces a non-interacting density matrix. Because of this limitation, one cannot obtain the exact \( \Pi(p) \) by the Fourier transformation of Kohn–Sham orbitals even if \( \rho(\mathbf{r}) \) is itself exact. A general strategy for improving the Kohn–Sham momentum density has been formulated by Lam and Platzman [51].

We computed Compton maps for \( ^1A_1 \) CH\(_2\) from the Kohn–Sham orbitals generated with two popular approximate density functionals: BLYP (gradient-corrected Becke’s exchange functional [55] paired with the gradient-corrected correlation functional of Lee et al. [56]) and B3LYP, a Becke-style three-parameter hybrid density functional [57]. Both functionals are frequently used in molecular calculations, and both are noted for their ability to produce highly accurate structural and energetic predictions for ground state species. For instance, the geometry of \( ^1A_1 \) CH\(_2\) optimized at the B3LYP/aug-cc-pVTZ level (\( r(CH) = 2.0961 \) \( a_0 \), \( \theta(HCH) = 101.95^\circ \)) is nearly identical with the essentially exact result of Comeau et al. [49].

Table 1 contains values of \( \langle p^2 \rangle \) and \( J(0) \) (for the three principal directions) evaluated from SCF, BLYP, B3LYP and MRSDCI density matrices. Compared with the SCF result, the MRSDCI, BLYP and B3LYP momentum distributions all exhibit a shift toward higher values of \( \langle p^2 \rangle \). At the same time, both BLYP and B3LYP distributions \( J(\mathbf{q}) \) have higher peak values than SCF along the \( p_z \) and \( p_\parallel \) directions, whereas the CI method predicts a lower peak in each case. Also, while the improvement of the wave function from SCF to CI barely affects the \( J_z(0) \) value (the \( p_z \) direction is along the \( C_2 \) symmetry axis), the BLYP and B3LYP calculations yield a smaller \( J_z(0) \).

In figure 6, we show the differences between Compton maps obtained in BLYP/B3LYP calculations and the corresponding SCF maps. The mixed results of Kohn–Sham calculations are apparent throughout the momentum space. The patterns of \( \delta J_{\text{BLYP}}(\mathbf{q}) \) and \( \delta J_{\text{B3LYP}}(\mathbf{q}) \) are quite similar, although deviations from the SCF map are considerably more pronounced for the BLYP functional. Against the CI Compton difference maps shown in figure 5(c) and (d), both BLYP and B3LYP methods change the SCF result in a manner which can hardly be called an improvement. Suffice it to say that \( \delta J_{\text{BLYP}}(\mathbf{q}) \) and \( \delta J_{\text{B3LYP}}(\mathbf{q}) \) are out of phase with \( \delta J_{\text{CI}}(\mathbf{q}) \) most of the time.

6. Conclusions

Compton maps present an informative description of the Compton profile function \( J(\mathbf{q}) \) as well as an interesting perspective on the electron momentum distribution. The closed form expression for \( J(\mathbf{q}) \) derived here makes evaluation of Compton maps relatively simple. Given a one-electron density matrix in a basis of Gauss-type orbitals, our algorithm has a fixed computational cost regardless of the complexity of the generator wave function.

Compton maps of individual molecules differ primarily in the low-momentum region. For higher values of \( |\mathbf{q}| \) the function \( J(\mathbf{q}) \) becomes essentially isotropic. Multivaluedness of \( J(\mathbf{q}) \) at zero momentum manifests
itself as a confluence of several contours drawn at different constant values.

Compton difference maps visualize the complex directional dependence of $J(q)$ on the quality of the position space wave function. In fact, in calculations of Compton profiles for ethylene employing a double-$\xi$ quality basis set, Tripathi et al. [46] found that electron correlation affects $J(q)$ to a greater extent than does the enlargement of the basis beyond double-$\xi$ quality in SCF calculations. As evidenced by the example of $^1A_1$ CH$_2$, going from the SCF method to BLYP or B3LYP has a mixed effect on the accuracy of Compton profiles. Overall, BLYP/B3LYP methods do not offer an improvement upon the SCF result.

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Ab initio Compton maps of small molecules


