

Phase-Space Approach to the Density-Functional Calculation of Compton Profiles of Atoms and Molecules

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The phase-space distribution function corresponding to a ground-state density of a many-electron system proposed earlier is explored as a means for generation of momentum-space properties through density-functional theory. Excellent results are found for the spherically averaged Compton profiles for several atoms and the molecules H_2 and N_2 , as well as the directional Compton profiles for N_2 , thereby providing both a useful scheme for computation of such profiles and confirmation of the basic theory. The entropy-maximization procedure employed is discussed from the point of view of information theory.

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In connection with a thermodynamic transcription of the density-functional theory of electronic structure,¹ there recently has been proposed a phase-space distribution function $f(\mathbf{r}, \mathbf{p})$ corresponding to a ground-state electron density $\rho(\mathbf{r})$. A unique $f(\mathbf{r}, \mathbf{p})$ was obtained by the invoking of an entropy-maximization principle, in analogy to the classical case. The resulting distribution function is Maxwellian in nature with a local temperature $T(\mathbf{r})$ and leads to various thermodynamic and fluid-theoretic equations for the electron cloud.^{1,2} In the present work, this same $f(\mathbf{r}, \mathbf{p})$, and a simple generalization of it, are used to predict momentum-space properties of an atom or molecule: the spherically averaged and directional Compton profiles.

Consider an N -electron system characterized by the ground-state density $\rho(\mathbf{r})$. Identify a phase-space distribution function $f(\mathbf{r}, \mathbf{p})$ with this density, and assume it to yield the correct kinetic energy density $t(\mathbf{r}, \rho)$ as well:

$$\rho(\mathbf{r}) = \int d^3p f(\mathbf{r}, \mathbf{p}), \quad \int d^3r \rho(\mathbf{r}) = N; \quad (1)$$

$$t(\mathbf{r}, \rho) = \frac{1}{2} \int d^3p p^2 f(\mathbf{r}, \mathbf{p}), \quad (2)$$

$$\int d^3r t(\mathbf{r}, \rho) = E_{\text{kin}}.$$

The most appropriate distribution function is then ob-

tained¹ by a maximization of the entropy defined as

$$S = \int d^3r s(\mathbf{r}), \quad s(\mathbf{r}) = -k \int d^3p f(\ln f - 1), \quad (3)$$

subject to the constraints of correct density [Eq. (1)] and correct kinetic energy density [Eq. (2)]. In Eq. (3), k is the Boltzmann constant. Introducing Lagrange multipliers $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ for the two constraints, respectively, one obtains

$$f(\mathbf{r}, \mathbf{p}) = \exp[-\alpha(\mathbf{r}) - \beta(\mathbf{r})p^2/2], \quad (4)$$

which, on evaluation of the Lagrange multipliers from Eqs. (1) and (2), becomes

$$f(\mathbf{r}, \mathbf{p}) = [2\pi kT(\mathbf{r})]^{-3/2} \rho(\mathbf{r}) \exp[-p^2/2kT(\mathbf{r})]. \quad (5)$$

Here $\beta(\mathbf{r}) = [kT(\mathbf{r})]^{-1}$, where the local temperature $T(\mathbf{r})$ is defined in analogy with the ideal-gas expression for kinetic energy by

$$\frac{3}{2} \rho(\mathbf{r}) kT(\mathbf{r}) = t(\mathbf{r}, \rho). \quad (6)$$

If we presume the validity of $f(\mathbf{r}, \mathbf{p})$ as a phase-space distribution function, the spherically averaged momentum density $\chi(\mathbf{p})$ is given by

$$\chi(\mathbf{p}) = \int d^3r f(\mathbf{r}, \mathbf{p}) = \int d^3r [\beta(\mathbf{r})/2\pi]^{3/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r})p^2/2], \quad (7)$$

and the spherically averaged Compton profile, within the impulse approximation, can be obtained from³

$$J(q) = \frac{1}{2} \int_{|q|}^{\infty} \chi(\mathbf{p}) p^{-1} d^3p = (2\pi)^{-1/2} \int d^3r \beta(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r})q^2/2], \quad (8)$$

which is a basic equation for calculation of the averaged Compton profiles of atomic and molecular systems.

Now consider the form of the kinetic energy density $t(\mathbf{r}, \rho)$ which defines $T(\mathbf{r})$ and $\beta(\mathbf{r})$ through Eq. (6). This kinetic energy density is not unique. The most natural form, adopted here, in terms of orbital densities $\{\rho_i\}$, is

$$t(\mathbf{r}, \rho) = \frac{1}{8} \sum_i \frac{\nabla \rho_i \cdot \nabla \rho_i}{\rho_i} - \frac{1}{8} \nabla^2 \rho. \quad (9)$$

Although the term $\nabla^2 \rho$ does not contribute to the global kinetic energy, it introduces quantum oscillations in the kinetic energy density. The choice of the coefficient $\frac{1}{8}$ in this term ensures that $T(\mathbf{r})$ will vanish at large distance and hopefully $T(\mathbf{r})$ then remains positive throughout the system. (No exceptions to this rule have been found.)

For the ground state of a hydrogen atom of nuclear charge Z , one has¹ $T(r) = Z/3kr$, and one obtains

from Eq. (8)

$$J(q) = Z^{-1} \left(\frac{675}{1024} \right)^{1/2} \left[1 + \frac{3}{4} (q/Z)^2 \right]^{-7/2}. \quad (10)$$

This compares favorably with, although it is not identical with, the exact result for this case,

$$J(q) = Z^{-1} (8/3\pi) \left[1 + (q/Z)^2 \right]^{-3}. \quad (11)$$

Should one omit the $\nabla^2 \rho$ terms in Eq. (9), on the other hand, the results are that $T(r) = Z^2/3k$ and $J(q)$ becomes a simple Gaussian, which is less accurate than Eq. (10).

$$f(\mathbf{r}, \mathbf{p}) = (2\pi)^{-3/2} [\beta_x(\mathbf{r})\beta_y(\mathbf{r})\beta_z(\mathbf{r})]^{1/2} \rho(\mathbf{r}) \exp \left[-\frac{1}{2} \{ \beta_x p_x^2 + \beta_y p_y^2 + \beta_z p_z^2 \} \right], \quad (13)$$

where β_x , β_y , and β_z are defined as

$$\beta_x(\mathbf{r}) = [kT_x(\mathbf{r})]^{-1}, \quad \frac{1}{2} \rho(\mathbf{r}) kT_x(\mathbf{r}) = t_x(\mathbf{r}), \quad \text{etc.} \quad (14)$$

The directional Compton profiles can now be defined as

$$J_{\hat{\mathbf{k}}}(q) = \int d^3p \chi(\mathbf{p}) \delta(\mathbf{q} - \mathbf{p} \cdot \hat{\mathbf{k}}), \quad (15)$$

where $\hat{\mathbf{k}}$ is a unit vector along the direction in which the Compton profile is to be evaluated. For a diatomic molecule the parallel (z direction) and the perpendicular components of the Compton profile are given by the expressions

$$J_{\parallel}(q) = (2\pi)^{-1/2} \int d^3r \beta_{\parallel}(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta_{\parallel}(\mathbf{r})q^2/2],$$

$$J_{\perp}(q) = (2\pi)^{-1/2} \int d^3r \beta_{\perp}(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta_{\perp}(\mathbf{r})q^2/2], \quad (16)$$

which can be compared with the spherically averaged Compton profile given by Eq. (8). The three directional temperatures or the β 's can be considered as the diagonal components of a kinetic-energy-density-related tensor.

Again there is arbitrariness in the definition of the kinetic energy density. The choice made here is

$$t_x(\mathbf{r}, \rho) = \frac{1}{8} \sum_i \frac{1}{\rho_i} \left(\frac{\partial \rho_i}{\partial x} \right)^2, \quad \text{etc.} \quad (17)$$

Each of t_x , t_y , and t_z is nonnegative everywhere. Terms $\frac{1}{8} \partial^2 \rho / \partial x^2$, are omitted because of tentative indications from numerical calculations that component kinetic energy densities so defined would go negative in some regions of a molecule.

Tables I and II compare the results of calculations by this method for atoms and molecules with results computed by the Hartree-Fock method. Compton profile $J(q)$ for atoms are given in Table I. First, for the hydrogen atom, Eq. (10) is compared with the exact Eq. (11). There is very little difference. Next, for the noble-gas atoms He through Xe, Eq. (8) is compared with the results of a full Fourier transformation of the numerical Hartree-Fock wave functions.⁴ In the present calculations, the Hartree-Fock wave functions of Clementi and Roetti were employed.⁵ Equation (8) is seen to give overall good accuracy, for the whole range of q , for all cases.

It may be noted that the phase-space distribution function $f(\mathbf{r}, \mathbf{p})$ of Eq. (5) depends only on scalar p ; it leads to only an averaged momentum density and Compton profile. To obtain the anisotropic momentum density and Compton profile, one can use a similar entropy-maximization procedure constrained to yield correct components of the kinetic energy density,

$$t_x(\mathbf{r}, \rho) = \frac{1}{2} \int \int \int dp_x dp_y dp_z p_x^2 f(\mathbf{r}, \mathbf{p}), \quad (12)$$

and similarly for the y and z components. Following the same lines, the final expression becomes

Results for two molecules, H_2 and N_2 , are presented in Table II. For H_2 , the averaged $J(q)$ as calculated from Eq. (8) with use of the Hartree-Fock wave function of Snyder and Basch⁶ shows close agreement with the $J(q)$ determined from Fourier transformation of the wave function as reported by Eisenberger.⁷ For N_2 , $J_{\text{av}}(q)$, $J_{\parallel}(q)$, and $J_{\perp}(q)$ computed from Eqs. (8) and (16) and the Hartree-Fock wave function⁶ are given together with the corresponding quantities obtained from Fourier transformation of the wave function by Tawil and Langhoff.⁸ Agreement is excellent.

The present phase-space approach to determine Compton profiles is a pure density-functional method, operating as it does with only the electron density. [The use of Hartree-Fock orbitals in the present paper is only a convenience; one could have as well employed Kohn-Sham orbitals (and kinetic energies), which are determined by the density.⁹] Fourier transformation of the Kohn-Sham orbitals is a density-functional scheme, too,¹⁰ but this method lacks rigor in that neither the wave function nor the single-particle density matrix is obtainable from the Kohn-Sham orbitals, so that their Fourier transformation does not give proper momentum-space orbitals.

A less accurate phase-space approach has existed for some time, based on the fact that direct calculation of momentum density from spatial electron density is

TABLE I. Compton profiles $J(q)$ for atoms.

q	H		He		Ne		Ar		Kr		Xe	
	Present ^a	Exact ^b	Present ^c	HF ^d	Present ^c	HF ^d	Present ^c	HF ^d	Present ^c	HF ^d	Present ^c	HF ^d
0.0	0.812	0.849	1.02	1.07	2.98	2.73	5.49	5.06	7.93	7.19	10.82	9.74
0.1	0.791	0.824	1.01	1.06	2.96	2.72	5.44	5.04	7.85	7.15	10.69	9.69
0.2	0.732	0.755	0.976	1.02	2.91	2.70	5.27	4.96	7.62	7.05	10.35	9.52
0.3	0.646	0.655	0.924	0.956	2.83	2.65	5.02	4.82	7.27	6.86	9.84	9.22
0.4	0.546	0.544	0.858	0.878	2.72	2.59	4.70	4.62	6.84	6.57	9.21	8.77
0.5	0.445	0.435	0.781	0.791	2.59	2.51	4.34	4.35	6.36	6.20	8.54	8.21
0.6	0.352	0.337	0.700	0.700	2.45	2.41	3.96	4.04	5.87	5.77	7.89	7.59
0.8	0.206	0.192	0.540	0.527	2.14	2.17	3.22	3.33	4.97	4.85	6.73	6.38
1.0	0.115	0.106	0.399	0.382	1.82	1.89	2.59	2.66	4.24	4.04	5.83	5.45
1.2	0.063	0.058	0.288	0.271	1.53	1.61	2.10	2.11	3.68	3.44	5.16	4.84
1.4	0.034	0.033	0.205	0.191	1.27	1.35	1.74	1.70	3.26	3.03	4.65	4.44
1.6	0.019	0.019	0.145	0.134	1.06	1.12	1.47	1.42	2.95	2.76	4.23	4.16
1.8	0.011	0.011	0.103	0.095	0.876	0.927	1.27	1.22	2.69	2.58	3.88	3.91
2.0	0.0063	0.0068	0.073	0.068	0.730	0.771	1.12	1.08	2.49	2.44	3.57	3.68
3.0	0.0006	0.0008	0.015	0.015	0.331	0.346	0.712	0.736	1.74	1.86	2.42	2.50
4.0	0.0001	0.0002	0.004	0.004	0.187	0.194	0.486	0.520	1.22	1.33	1.72	1.71
5.0	0.0000	0.0000	0.001	0.001	0.123	0.124	0.333	0.359	0.873	0.933	1.30	1.30
10.0	0.0000	0.0000	0.000	0.000	0.024	0.022	0.073	0.075	0.246	0.260	0.470	0.510

^aEquation (10) of text.

^bEquation (11) of text.

^cEquation (8) of text, wave functions from Ref. 5.

^dReference 4; numerical Hartree-Fock wave functions.

possible in certain special cases. One such transformation¹¹ is exact for a homogeneous electron gas, while another¹² corresponds to a gas of almost constant density. Recent revival of interest in the first procedure is due to the improved numerical results¹³ that it yields for the Compton profiles when evaluated with a good quality (e.g., Hartree-Fock) density instead of a Thomas-Fermi density, although the theory is essentially based on a quasiclassical phase-space consideration of the Thomas-Fermi theory. Of all methods for computing Compton profiles, the present phase-space approach is the easiest to carry through. Neither the momentum density of Eq. (7) nor that of other semiclassical methods has the correct asymptotic behavior as $p \rightarrow \infty$.

TABLE II. Compton profiles for H₂ and N₂.

q	$J_{av}(q)$ for H ₂		$J_{av}(q)$ for N ₂		$J_{ }(q)$ for N ₂		$J_{\perp}(q)$ for N ₂	
	Present ^a	HF ^b	Present ^c	HF ^d	Present ^e	HF ^d	Present ^e	HF ^d
0.0	1.48	1.56	5.74	5.29	6.18	6.08	5.05	5.27
0.1	1.45	1.52	5.68	5.25	6.09	5.98	5.01	5.23
0.2	1.37	1.41	5.50	5.14	5.85	5.69	4.90	5.13
0.3	1.24	1.26	5.22	4.95	5.48	5.26	4.73	4.96
0.4	1.08	1.07	4.86	4.70	5.02	4.75	4.50	4.71
0.5	0.909	0.887	4.46	4.39	4.53	4.23	4.23	4.41
0.6	0.744	0.713	4.03	4.03	4.04	3.72	3.94	4.06
0.8	0.462	0.433	3.18	3.27	3.14	2.89	3.30	3.28
1.0	0.267	0.250	2.45	2.56	2.40	2.27	2.67	2.54
1.2	0.148	0.142	1.86	1.96	1.83	1.82	2.11	1.94
1.4	0.082	0.080	1.42	1.51	1.40	1.47	1.64	1.49
1.6	0.045	0.045	1.11	1.17	1.09	1.19	1.26	1.16
1.8	0.026	0.026	0.880	0.925	0.860	0.968	0.983	0.927
2.0	0.015	0.015	0.721	0.749	0.695	0.792	0.779	0.759
3.0	0.0017		0.372	0.376	0.322	0.370	0.365	0.380
4.0	0.0003		0.237	0.235	0.198	0.232	0.244	0.235
5.0	0.0000		0.154	0.148	0.134	0.153	0.169	0.147
10.0	0.0000		0.017		0.022		0.019	

^aEquation (8) of text; double-zeta self-consistent-field (SCF) wave function from Ref. 6.

^bReference 7.

^cEquation (8) of text; double-zeta SCF wave function from Ref. 6.

^dReference 8.

^eEquation (16) of text, double-zeta SCF wave function from Ref. 6.

momentum density of Eq. (7) nor that of other semiclassical methods has the correct asymptotic behavior as $p \rightarrow \infty$.

Justification for what has been done here, and justification for the antecedent works,^{1,2} may be given from the fundamental theorem of information theory.¹⁴ In order to predict a distribution $\chi(\mathbf{p}) = \int d^3r f(\mathbf{r}, \mathbf{p})$ from a distribution $f(\mathbf{r}, \mathbf{p})$, the problem was to find the most appropriate $f(\mathbf{r}, \mathbf{p})$ satisfying two constraints, that $\int d^3p f(\mathbf{r}, \mathbf{p}) = \rho(\mathbf{r})$, where $\rho(\mathbf{r})$ is a given distribution, and $\int d^3p (p^2/2) \times f(\mathbf{r}, \mathbf{p}) = t(\mathbf{r}, \rho)$, where $T(\mathbf{r}, \rho)$ is also given and is everywhere positive. What was done to solve this problem was just what information theory says will give the least-biased $f(r, p)$: Maximize $S = -k \int d^3r \times \int d^3p f (\ln f - 1)$ subject to the two constraints.¹⁵ The result is not the exact quantum-mechanical $f(r, p)$, as the difference between Eqs. (10) and (11) shows. But it is amazingly accurate.

Physical intuition would suggest that $\rho(\mathbf{r})$ and $t(\mathbf{r}, \rho)$ should contain a lot of information about momentum space. That is why the Compton profiles predicted in the present paper are so good. Greater accuracy can be achieved through the incorporation of more constraints, as the use of the Cartesian components of t in this paper has shown. But information theory provides a basis for the thermodynamic description of the previous works^{1,2}: Demand that an $f(\mathbf{r}, \mathbf{p})$ exists, optimally packed with suitable information, and a classical picture at once emerges.

Elsewhere it has been demonstrated that this same phase-space approach leads to a compact and useful formula for the exchange-energy functional for atoms.¹⁶

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