

Quantum chemistry in phase space: Some current trends

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Abstract. Recent developments in the phase space formalisms within density functional theory are discussed. The phase space distribution function corresponding to a ground state electron density, obtained through an entropy maximization procedure, leads to good quality momentum density and first order reduced density matrix. Calculations of Compton profiles and exchange energies with different kinetic energy functionals show interesting results.

Keywords. Density functional theory; phase space distribution function; momentum density; Compton profile; exchange energy; information theory; local thermodynamics.

1. Introduction

Quantum mechanical description of a many-electron system is usually based on the configuration space wavefunction $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ or the electron density $\rho(\mathbf{r})$ (Bamzai and Deb 1981; Ghosh and Deb 1982; Parr 1983; March and Deb 1987) and only occasionally on the momentum space wavefunction $\chi(\mathbf{p}_1, \dots, \mathbf{p}_N)$ or the momentum density $\gamma(\mathbf{p})$ (Epstein 1973). Although either of the two spaces can provide the framework for a complete description, there has been an increasing interest recently in the phase space (PS) representation (Hillery *et al* 1984) of quantum mechanics. Apart from the redundancy, the PS language has been questioned also for apparent contradictions with the quantum mechanical uncertainty principle. These objections have however mostly been resolved and the PS approach has been highly useful in many applications viz photodissociation (Brown and Heller 1981), collisions (Carruthers and Zachariassen 1983), intra-molecular energy transfer (Hutchinson and Wyatt 1980) etc.

The PS distribution function was first introduced in quantum mechanics by Wigner (1932) and subsequently generalized by Moyal (1949) and others (see Hillery *et al* 1984 for a review). Wigner's PS function in reduced space is merely a particular representation of the reduced density matrix but, has the additional advantage of being able to provide a classical-like appearance to the formalism. This makes the nature of the quantum corrections transparent and thus the PS approach has a unique strength for semiclassical applications (Heller 1976).

Being a direct product of the position space and the momentum space, the phase space can also establish a bridge between these two spaces. The wavefunctions $\psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ and $\chi(\mathbf{p}_1, \dots, \mathbf{p}_N)$ are related simply by a Dirac-Fourier transform but the exact relationship between the two single-particle densities $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$ is still unknown. Using the six-dimensional PS distribution function $f(\mathbf{r}, \mathbf{p})$ as an intermediate quantity, approximate but accurate transformations between the electron density and the momentum density (Parr *et al* 1986) have however been

suggested. In this paper, we discuss the current status of these prescriptions for interconnecting $\rho(\mathbf{r})$ and $\gamma(\mathbf{p})$. The resulting $f(\mathbf{r}, \mathbf{p})$ is also shown to lead to a good approximation to the first-order density matrix $\rho_1(\mathbf{r}; \mathbf{r}')$ and hence the exchange energy functional (Ghosh and Parr 1986) of the density functional theory (DFT) (Kohn and Sham 1965; Ghosh and Deb 1982; Parr 1983).

2. Formalism

The Wigner distribution function for a single particle system is defined as

$$f(\mathbf{r}, \mathbf{p}) = (2\pi)^{-3} \int \psi^*(\mathbf{r} + \mathbf{s}/2) \psi(\mathbf{r} - \mathbf{s}/2) \exp[-i\mathbf{p} \cdot \mathbf{s}] d\mathbf{s}. \quad (1)$$

For an N -particle system, a six-dimensional $f(\mathbf{r}, \mathbf{p})$ can be defined in terms of the first-order reduced density matrix $\rho_1(\mathbf{r}; \mathbf{r}')$, viz,

$$f(\mathbf{r}, \mathbf{p}) = (2\pi)^{-3} \int \rho_1(\mathbf{r} + \mathbf{s}/2; \mathbf{r} - \mathbf{s}/2) \exp[-i\mathbf{p} \cdot \mathbf{s}] d\mathbf{s}. \quad (2)$$

A reverse transform of (2) yields the density matrix $\rho_1(\mathbf{r}; \mathbf{r}')$ from $f(\mathbf{r}, \mathbf{p})$. The function $f(\mathbf{r}, \mathbf{p})$ also satisfies the marginal conditions:

$$\int f(\mathbf{r}, \mathbf{p}) d\mathbf{p} = \rho(\mathbf{r}), \quad (3a)$$

$$\int f(\mathbf{r}, \mathbf{p}) d\mathbf{r} = \gamma(\mathbf{p}). \quad (3b)$$

The definition of a PS function is however not unique and a class of PS functions satisfying the marginals (3) is possible (Cohen 1966). Equation (3) however suggests that the construction of an appropriate $f(\mathbf{r}, \mathbf{p})$ from $\rho(\mathbf{r})$ should provide a route for generating $\gamma(\mathbf{p})$ from $\rho(\mathbf{r})$.

The simplest $f(\mathbf{r}, \mathbf{p})$ constructed from $\rho(\mathbf{r})$ corresponds to the Thomas Fermi (TF) approximation and is given by

$$f(\mathbf{r}, \mathbf{p}) = 2(2\pi)^{-3} \Theta[p_F^2(\mathbf{r}) - p^2], \quad (4)$$

where $p_F(\mathbf{r})$ is the Fermi momentum at position \mathbf{r} and Θ is the Heaviside theta function. Integration over \mathbf{p} leads to the well-known TF relation

$$\rho(\mathbf{r}) = (3\pi^2)^{-1} p_F^3(\mathbf{r}). \quad (5)$$

The expectation value $\langle p^n \rangle$ obtained from (4) is:

$$\begin{aligned} \int \int p^n f(\mathbf{r}, \mathbf{p}) d\mathbf{p} d\mathbf{r} &= (4\pi^3)^{-1} \int \int p^n \Theta[p_F^2(\mathbf{r}) - p^2] d\mathbf{p} d\mathbf{r} \\ &= [\pi^2(n+3)]^{-1} \int p_F^{n+3}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (6)$$

On using (3) and (5), (6) becomes

$$\int p^n \gamma(\mathbf{p}) d\mathbf{p} = [3/(n+3)] (3\pi^2)^{n/3} \int \rho^{(n+3)/3} d\mathbf{r}. \quad (7)$$

Equation (7) is the well-known Coulson and March (1950) relation interconnecting electron density and momentum density expectation values and has been extensively used by Gadre and Pathak (1981) and Pathak *et al* (1984) for calculations on atomic and molecular systems. It can however transform only a restricted class of density functionals in position space (of the form $\rho^{1+n/3}$) to those in momentum space.

A generalization can be obtained by evaluating the expectation value of an arbitrary function $g(p)$, viz,

$$\begin{aligned}\iint g(p) f(\mathbf{r}, \mathbf{p}) d\mathbf{p} d\mathbf{r} &= (4\pi^3)^{-1} \iint g(p) \Theta[p_F^2(\mathbf{r}) - p^2] d\mathbf{p} d\mathbf{r} \\ &= (1/\pi^2) \int h[p_F(\mathbf{r})] d\mathbf{r},\end{aligned}\quad (8)$$

where

$$h(p_F) = \int g(p) p^2 d\mathbf{p}; \quad g(p) = (1/p^2) dh(p)/dp. \quad (9)$$

The generalized Coulson-March relationship is thus given by

$$\int g(p) \gamma(p) dp = (1/\pi^2) \int h(p_F(\mathbf{r})) d\mathbf{r}, \quad (10)$$

and can be employed to transform any position space density functional to a momentum space one by first rewriting it as a function of $p_F(\mathbf{r})$ using $p_F(\mathbf{r}) = (3\pi^2\rho)^{1/3}$ and then using (9). Equation (10) has been recently obtained by Das and Ghosh (1987) and Das *et al* (1987) who have also used it to derive a correlation energy functional in momentum space.

An alternative information-theoretic approach to obtain an $f(\mathbf{r}, \mathbf{p})$ corresponding to the density $\rho(\mathbf{r})$ has recently been proposed in connection with a thermodynamic transcription of density functional theory (Ghosh *et al* 1984; Ghosh and Berkowitz 1985). Assuming the PS function to yield the correct density $\rho(\mathbf{r})$ and kinetic energy (KE) density $t(\mathbf{r}, \rho)$, viz,

$$\int f(\mathbf{r}, \mathbf{p}) d\mathbf{p} = \rho(\mathbf{r}); \quad \int f(\mathbf{r}, \mathbf{p}) (p^2/2) d\mathbf{p} = t(\mathbf{r}, \rho), \quad (11)$$

the most appropriate distribution function is obtained through a maximization of the entropy functional defined as

$$S = -k \iint f[\ln f - 1] d\mathbf{p} d\mathbf{r}, \quad (12)$$

where k is the Boltzmann constant. The resulting PS function is given by

$$f(\mathbf{r}, p) = [\beta(\mathbf{r})/2\pi]^{3/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r}) p^2/2], \quad (13)$$

where $\beta(\mathbf{r})$ is the Lagrange multiplier to the KE constraint and is given by $\beta(\mathbf{r}) = (3/2)\rho(\mathbf{r})/t(\mathbf{r}, \rho) = 1/kT(\mathbf{r})$. Here $T(\mathbf{r})$ is the local temperature defined in analogy with the ideal gas expression for KE, viz, $(3/2)\rho(\mathbf{r})kT(\mathbf{r}) = t(\mathbf{r}, \rho)$.

The spherically averaged momentum density $\gamma(p)$ and the Compton profile $J(q)$ are now given by (Parr *et al* 1986)

$$\gamma(p) = \int f(\mathbf{r}, \mathbf{p}) d\mathbf{r} = \int d\mathbf{r} [\beta(\mathbf{r})/2\pi]^{3/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r}) p^2/2], \quad (14)$$

and

$$\begin{aligned}J(q) &= (1/2) \int \gamma(p) (1/p) dp \\ &= (2\pi)^{-1/2} \int d\mathbf{r} \beta(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta(\mathbf{r}) q^2/2].\end{aligned}\quad (15)$$

A reverse transform of (2) applied to $f(\mathbf{r}, p)$ of (13) yields the first-order density matrix

$$\rho_1(\mathbf{r} + \mathbf{s}/2; \mathbf{r} - \mathbf{s}/2) = \rho(\mathbf{r}) \exp[-s^2/2\beta(\mathbf{r})], \quad (16)$$

which leads to the exchange energy density functional

$$\begin{aligned}
E_x[\rho] &= -(1/4) \int \int d\mathbf{r} d\mathbf{r}' |\mathbf{r} - \mathbf{r}'|^{-1} |\rho_1(\mathbf{r}; \mathbf{r}')|^2 \\
&= -(\pi/2) \int \rho(\mathbf{r})^2 \beta(\mathbf{r}) d\mathbf{r}.
\end{aligned} \tag{17}$$

Equations (14) and (15) form the basis for the prediction of the momentum space properties while (16) and (17) can be used to obtain the density matrix and the exchange energy from the electron density. The quantity $\beta(\mathbf{r})$ can be calculated from a suitable functional form for the kinetic energy density. Ghosh *et al* (1984), Parr *et al* (1986) and Ghosh and Parr (1986) made use of the orbital density form:

$$t(\mathbf{r}, \rho) = (1/8) \Sigma (\nabla \rho_i \cdot \nabla \rho_i) / \rho_i - (1/8) \nabla^2 \rho. \tag{18}$$

One can however employ the TF expression

$$t_0(\mathbf{r}, \rho) = (3/10) (3\pi^2)^{2/3} \rho(\mathbf{r})^{5/3}, \tag{19}$$

or the gradient corrected result

$$t(\mathbf{r}, \rho) = t_0(\mathbf{r}, \rho) + (1/72) (\nabla \rho \cdot \nabla \rho) / \rho. \tag{20}$$

Although the Laplacian term of (18) does not contribute to the integrated result, it is however responsible for some interesting consequences (Yang 1986; Yang *et al* 1986). The coefficient (1/8) of the Laplacian has been shown to arise naturally from a density matrix expansion by Berkowitz (1986).

It is interesting to note that using $\beta(\mathbf{r})$ based on TF KE (19), one obtains from (17) the Dirac exchange formula with a factor (10/9). This leads to a value of $\alpha = (10/9) (2/3) = 0.74$ which is the mean of the α values for atoms viz 0.77 for He and 0.70 for Xe in X_α theory (Gopinathan *et al* 1976). Using (20) for calculating $\beta(\mathbf{r})$, one is led to a gradient correction for the exchange energy functional. Analogously, a connection with the Coulson-March formula (7) for the Compton profile can be established from (15) by using TF KE (19) for obtaining $\beta(\mathbf{r})$.

The TF based results can predict only spherically averaged momentum space properties. The PS function of (13) can however be generalized to enable prediction of anisotropy in momentum density (Parr *et al* 1986). Using the KE component densities $t_x(\mathbf{r}, \rho)$, $t_y(\mathbf{r}, \rho)$ and $t_z(\mathbf{r}, \rho)$ as constraints, the resulting PS function becomes

$$\begin{aligned}
f(\mathbf{r}, \mathbf{p}) &= (2\pi)^{-3/2} [\beta_x(\mathbf{r}) \beta_y(\mathbf{r}) \beta_z(\mathbf{r})]^{1/2} \rho(\mathbf{r}) \\
&\quad \exp[-(1/2) \{\beta_x p_x^2 + \beta_y p_y^2 + \beta_z p_z^2\}],
\end{aligned} \tag{21}$$

where $\beta_x(\mathbf{r})$, $\beta_y(\mathbf{r})$ and $\beta_z(\mathbf{r})$ are the respective Lagrange multipliers for the three constraints. For a diatomic molecule, this leads to the expressions for the directional (parallel and perpendicular) Compton profiles:

$$J_{\parallel}(q) = (2\pi)^{-1/2} \int d\mathbf{r} \beta_{\parallel}(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta_{\parallel}(\mathbf{r}) q^2/2], \tag{22a}$$

$$J_{\perp}(q) = (2\pi)^{-1/2} \int d\mathbf{r} \beta_{\perp}(\mathbf{r})^{1/2} \rho(\mathbf{r}) \exp[-\beta_{\perp}(\mathbf{r}) q^2/2]. \tag{22b}$$

The exchange energy functional of (17) however has been shown (Kemister 1986) to remain unchanged by this generalization and hence is applicable to atoms and molecules alike.

3. Results and discussion

The numerical results evaluated through (15) and (17) for the Compton profiles (Parr *et al* 1986) and the exchange energies respectively (Ghosh and Parr 1986) by using the Hartree-Fock density (Clementi and Roetti 1974) for noble gas atoms show good agreement with the actual ones. The directional Compton profiles from (22) also agree very well with the Hartree-Fock results for the N₂ molecule (Parr *et al* 1986).

In these calculations, the KE functional of (18) has been employed for obtaining $\beta(\mathbf{r})$. This is especially convenient when one does a Kohn and Sham (1965) type calculation which gives density through the orbital densities. The exchange potential corresponding to the exchange energy functional of (17) with $\beta(\mathbf{r})$ defined through (18) can then be directly incorporated in the self consistent scheme.

It is interesting to study the effect of using other approximate KE density functionals [e.g. (19) or (20)] for obtaining $\beta(\mathbf{r})$ in the calculations. Some illustrative numerical results of such calculations using (20) are presented for the Compton profiles and exchange energies respectively in tables 1 and 2 for the atoms

Table 1. Compton profiles $J(q)$ for atoms.

q	Ne					Ar				
	PRG ^a	PRGwL ^b	TFW ^c	TFWL ^d	HF ^e	PRG ^a	PRGwL ^b	TFW ^c	TFWL ^d	HF ^e
0.0	2.98	2.50	3.15	3.43	2.73	5.49	4.78	5.82	6.28	5.06
0.2	2.91	2.47	3.03	3.18	2.70	5.27	4.66	5.49	5.66	4.96
0.4	2.72	2.38	2.74	2.76	2.59	4.70	4.33	4.74	4.71	4.62
0.6	2.45	2.24	2.39	2.36	2.41	3.96	3.84	3.91	3.86	4.04
0.8	2.14	2.06	2.05	2.01	2.17	3.22	3.28	3.19	3.16	3.33
1.0	1.82	1.86	1.75	1.71	1.89	2.59	2.72	2.60	2.58	2.66
1.2	1.53	1.64	1.48	1.45	1.61	2.10	2.22	2.13	2.13	2.11
1.6	1.06	1.22	1.07	1.05	1.12	1.47	1.49	1.49	1.48	1.42
2.0	0.730	0.855	0.770	0.761	0.771	1.12	1.11	1.10	1.09	1.08
3.0	0.331	0.347	0.349	0.347	0.346	0.712	0.740	0.668	0.654	0.736
5.0	0.123	0.131	0.107	0.103	0.124	0.333	0.376	0.335	0.330	0.359
10.0	0.024	0.031	0.024	0.024	0.022	0.073	0.078	0.069	0.068	0.075

^a Equations (15) and (18) of text: results from Parr *et al* (1986); ^b equations (15) and (18) of text; but without the Laplacian term in the latter; ^c equations (15) and (20) of text; ^d equations (15) and (20) of text; but with an additional $(-1/72)\nabla^2\rho$ term in the latter; ^e results from Biggs *et al* (1975): numerical Hartree-Fock wavefunctions.

Table 2. Exchange energies for atoms.

Atoms	Exact ^a exchange	GP ^b exchange	GPwL ^c exchange	TFW ^d exchange	TFWL ^e exchange
Ne	12.11	11.57	12.81	11.23	11.51
Ar	30.18	29.24	31.70	28.86	29.51

^a Results from Perdew (1985); ^b equations (17) and (18) of text; results from Ghosh and Parr (1986); ^c equations (17) and (18) of text; but without the Laplacian term in the latter; ^d equations (17) and (20) of text; ^e equations (17) and (20) of text; but with an additional $(-1/72)\nabla^2\rho$ term in the latter.

Ne and Ar. Calculations have been made with and without the inclusion of the Laplacian term, which however makes the KE density nonunique. The results indicate that this term plays an important role in the present prescription. It may be noted that the coefficients of the Laplacian term are taken as (1/8) and (1/72) for (18) and (20) respectively to ensure positivity of the resulting KE density at least for atomic systems.

The numerical results on Compton profiles as well as the exchange energies for the approximate KE functional (20) seem to be less accurate. This is perhaps a consequence of the poor local behaviour of these functionals although they show good accuracy for the global KE values for atomic (Ghosh and Balbas 1985; Ghosh and Parr 1985) as well as molecular systems (Allan *et al* 1985; Deb and Chattaraj 1986; Lee and Ghosh 1986). Better KE functionals with proper local behaviour (Deb and Ghosh 1983; Chattaraj and Deb 1984; Ghosh and Balbas 1985; Ghosh and Parr 1985; Yang *et al* 1986) are however expected to yield better results.

4. Concluding remarks

The present paper discusses the PS approach from the point of view of its use as a calculational tool e.g. for establishing a bridge between the position space and momentum space. The PS function that has been obtained here through an entropy maximization (Levine and Tribus 1979) has recently been shown (Berkowitz 1986) to be a well-defined approximation to the Wigner distribution function. The present PS function also leads to a local thermodynamic transcription (Ghosh *et al* 1984) and a classical fluid-like approach (Ghosh and Berkowitz 1985) corresponding to the ground state DFT. A dynamical extension is also possible through the time-dependent DFT (Deb and Ghosh 1982; Runge and Gross 1984; Bartolotti 1986; Dhara and Ghosh 1987) which gives new insight into the collision phenomena (Deb and Chattaraj 1987).

The PS approach in general can be very helpful in understanding the connections between classical and quantum mechanics. Here a dynamical variable is represented by an ordinary function of \mathbf{r} and \mathbf{p} and the quantum mechanical averages are evaluated just like in a classical case. Another distinctive feature is that both the state and the transition can be handled in an equivalent manner. The PS formalism is also useful in deriving the equations of quantum fluid dynamics (Deb and Ghosh 1987).

The DFT in terms of $\rho(\mathbf{r})$ is well established and sufficient interest is generated for DFT in momentum space as well in terms of $\gamma(\mathbf{p})$. An alternative formulation of DFT is however possible in phase space in terms of $f(\mathbf{r}, \mathbf{p})$; this might be of special importance in dealing with time-dependent phenomena. The understanding of chemical binding is considerably enhanced through studies of contour maps of electron density (Bamzai and Deb 1981) as well as momentum density (Koga *et al* 1985 and references therein). Studies on $f(\mathbf{r}, \mathbf{p})$ for simple atomic (Dahl and Springborg 1982) and molecular (Springborg 1983) systems have started only recently and seem to be a valuable approach for understanding physicochemical phenomena.

Acknowledgements

It is a pleasure to thank Professors Robert G Parr and Max Berkowitz for many helpful discussions. I am grateful to Professor B M Deb for his constant encouragement and advice.

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