Phase Space View of Ensembles of Excited States

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Abstract: The density functional theory and its extension to ensembles of excited states can be formalized as thermodynamics. However, these theories are not unique because one of their key quantities, the kinetic energy density, can be defined in several ways. Usually, the everywhere positive gradient form is applied; however, other forms are also acceptable, provided they integrate to the true kinetic energy. Recently, a kinetic energy density of the ground-state theory maximizing the information entropy has been proposed. Here, ensemble kinetic energy density, leading to extremum information entropy, is derived via constrained search. The corresponding ensemble temperature is found to be constant.

Key Words: Ensemble of excited states; Kinetic energy density; Constrained search; Ensemble temperature

1 Introduction

Density functional theory¹ is a ground state theory. It is valid for the lowest-energy state in each symmetry class^{2,3}. The theory was first rigorously generalized for excited states by Theophilou⁴. It was further generalized by Gross, Oliveira and Kohn⁵. The method was used in several calculations^{6–12}. The relativistic generalization of this formalism has also been done¹³. The optimized potential method was also extended to ensembles of excited states¹⁴. We mention by passing that theories for a single excited state also exists^{14–21}. An alternative theory, worth remarking, is time-dependent density functional theory^{22,23}.

The ground-state density functional theory was formalized as ‘thermodynamics’ by Ghosh, Berkowitz and Parr²⁴. A phase-space distribution function $f(\mathbf{r}, \mathbf{p})$ was derived by maximizing a phase-space Shannon information entropy subject to the conditions that f yields the density and the local kinetic energy density of the system. A local Maxwell-Boltzmann distribution function was resulted and the concept of local temperature was introduced. This phase-space description resulted several applications^{25–29}. Extensions of the formalism have also been provided^{30–40}. A couple of years ago the local thermodynamic formalism was extended to ensembles of excited states⁴¹ and ensemble local temperature was defined.

Recently the ground-state theory has been revisited⁴². The local temperature of the Ghosh-Berkowitz-Parr theory was defined *via* the kinetic energy density. However, the kinetic

energy density is not uniquely defined. Usually the everywhere positive gradient form is applied, though any function that integrates to the true kinetic energy can do. It has recently been shown⁴² that it is possible selecting the kinetic energy density so that the local temperature be a constant for the whole system under consideration. Moreover, it turned out that the kinetic energy density corresponding to the constant temperature, maximizes the information entropy.

The ensemble kinetic energy density is not defined uniquely either. In this paper the ensemble temperature and kinetic energy density resulting the maximum phase-space information entropy are presented. The extremum is obtained by the constrained search of Levy and Lieb^{43,44}.

The outline of this paper is as follows: In Section 2 the ensemble theory of excited states is summarized. In Section 3 the local thermodynamic formalism of ensembles is reviewed⁴¹. The constrained search is applied in Section 4 to obtain the ensemble kinetic energy density giving the maximum phase-space information entropy. Section 5 is devoted to an illustrative example and discussion.

2 Ensemble density functional theory for excited states

The Schrödinger equations of the Hamiltonian $\hat{H}$ can be written as

$$\hat{H}\Psi_i = E_i\Psi_i \quad (i = 1, \dots, M) \quad (1)$$

where

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$$E_1 \leq E_2 \leq \dots \quad (2)$$

are the energy eigenvalues. The ensemble energy is defined as ⁵

$$\mathcal{E} = \sum_{i=1}^M w_i E_i, \quad (3)$$

where $w_1 \geq w_2 \geq \dots \geq w_M \geq 0$. When the weighting factors are $w_i = 1/M$ the eigenensemble of M states is obtained. It corresponds to the subspace theory of Theophilou ⁴.

The generalized Hohenberg-Kohn-theorems for ensembles read as follows:

(i) The external potential $v(\mathbf{r})$ is determined within a trivial additive constant, by the ensemble density n defined as

$$n = \sum_{i=1}^M w_i n_i. \quad (4)$$

(ii) For a trial ensemble density $n'(\mathbf{r})$ such that

$$n'(\mathbf{r}) \geq 0 \quad (5)$$

and

$$\int n'(\mathbf{r}) d\mathbf{r} = N, \quad (6)$$

it holds that

$$\mathcal{E}[n] \leq \mathcal{E}[n']. \quad (7)$$

The ensemble functional $\mathcal{E}$ has its minimum at the correct ensemble density n . The variation principle leads to the Euler-equation:

$$\frac{\delta \mathcal{E}}{\delta n} = \mu. \quad (8)$$

The ensemble Kohn-Sham equations were also derived:

$$\left[-\frac{1}{2} \nabla^2 + v_{\text{KS}} \right] u_i(\mathbf{r}) = \varepsilon_i u_i(\mathbf{r}). \quad (9)$$

The ensemble Kohn-Sham potential

$$v_{\text{KS}}(\mathbf{r}; n) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{\text{xc}}(\mathbf{r}; w, n) \quad (10)$$

is a functional of the ensemble density n . The ensemble exchange-correlation potential v_{xc} is the functional derivative of the ensemble exchange-correlation energy functional E_{xc} .

3 A “thermodynamical” view of ensembles of excited states

Now, the thermodynamical transcription of ensembles is summarized ⁴¹. Consider a system of N electrons in a local external potential $v(\mathbf{r})$. The ensemble is specified by a phase-space distribution function $f(\mathbf{r}, \mathbf{p})$ that satisfies

$$\int d\mathbf{p} f(\mathbf{r}, \mathbf{p}) = n(\mathbf{r}), \quad (11)$$

$$\int d\mathbf{r} n(\mathbf{r}) = N, \quad (12)$$

and

$$\int d\mathbf{p} \frac{p^2}{2m} f(\mathbf{r}, \mathbf{p}) = t_s(\mathbf{r}). \quad (13)$$

m is the mass. The ensemble non-interacting kinetic energy density $t_s(\mathbf{r})$ integrates to the ensemble non-interacting kinetic energy $\mathcal{E}_{\text{kin}}$

$$\mathcal{E}_{\text{kin}} = \int d\mathbf{r} t_s(\mathbf{r}). \quad (14)$$

There exist several distribution functions that satisfy the marginal conditions (11)–(13). One can choose a distribution function maximizing the entropy

$$S = \int d\mathbf{r} s(\mathbf{r}), \quad (15)$$

$$s(\mathbf{r}) = -k \int d\mathbf{p} f(\ln f - 1) \quad (16)$$

subject to the constraints of correct density (Eq.(11)) and correct non-interacting kinetic energy (Eq.(13)). k is the Boltzmann constant. The maximum entropy is a local Maxwell-Boltzmann distribution function

$$f(\mathbf{r}, \mathbf{p}) = e^{-\alpha(\mathbf{r})} e^{-\beta(\mathbf{r}) p^2 / 2m}, \quad (17)$$

where $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ are $\mathbf{r}$ -dependent Lagrange multipliers. Eq.(13) then leads to

$$t_s(\mathbf{r}) = \frac{3}{2} \frac{n(\mathbf{r})}{\beta(\mathbf{r})}. \quad (18)$$

One can immediately see that it can be rewritten as an ideal gas expression

$$t_s(\mathbf{r}) = \frac{3}{2} n(\mathbf{r}) k T(\mathbf{r}), \quad (19)$$

where the local temperature $T(\mathbf{r})$ is defined as

$$T(\mathbf{r}) = \frac{1}{k\beta(\mathbf{r})}. \quad (20)$$

Then the Maxwell-Boltzmann distribution function takes the form

$$f(\mathbf{r}, \mathbf{p}) = [2\pi m k T(\mathbf{r})]^{-3/2} n(\mathbf{r}) e^{-p^2 / 2m k T(\mathbf{r})}. \quad (21)$$

Substituting Eq.(21) into Eq.(15) we arrive at the well-known Sackur–Tetrode expression of the entropy:

$$S = -k \int d\mathbf{r} n(\mathbf{r}) \ln n(\mathbf{r}) + \frac{1}{2} k \int d\mathbf{r} n(\mathbf{r}) [3 \ln (2\pi m k T) + 5]. \quad (22)$$

The distribution function can also be formulated as

$$f(\mathbf{r}, \mathbf{p}) = e^{\mu / k T(\mathbf{r})} e^{-(p^2 / 2m + v_{\text{eff}}) / k T(\mathbf{r})}, \quad (23)$$

where

$$v_{\text{eff}} = \mu - \frac{\ln (\lambda^3 n)}{\beta} \quad (24)$$

and

$$\lambda = (2\pi mkT)^{-1/2}. \quad (25)$$

The effective potential v_{eff} can be related to the ensemble Kohn-Sham potential.

4 Maximum information entropy with constrained search

In the previous section the information entropy was maximized with constraints (11)–(13). However, the ensemble kinetic energy density in Eq.(13) is not uniquely defined. Therefore the ensemble temperature is not unique either. Only the ensemble non-interacting kinetic energy $\mathcal{E}_{\text{kin}}$ in Eq.(14) is fixed. Any function that integrates to $\mathcal{E}_{\text{kin}}$ is a possible applicant for the ensemble non-interacting kinetic energy density, though functions everywhere positive are preferred.

Now we select that ensemble temperature (or ensemble non-interacting kinetic energy density) that maximizes information entropy. We are going to find the phase-space distribution function $f(\mathbf{r}, \mathbf{p})$ that satisfies

$$\int d\mathbf{p} f(\mathbf{r}, \mathbf{p}) = n(\mathbf{r}), \quad (26)$$

$$\int d\mathbf{r} n(\mathbf{r}) = N \quad (27)$$

and

$$\int d\mathbf{r} d\mathbf{p} \frac{p^2}{2m} f(\mathbf{r}, \mathbf{p}) = \int d\mathbf{r} t_s(\mathbf{r}) = \mathcal{E}_{\text{kin}}. \quad (28)$$

The constrained search of Levy and Lieb^{43,44} is applied. That is, the extremum is pursued in two steps. In the first step the search is over all distribution functions that result a given ensemble temperature. In the second step the search is over all temperatures. We can immediately notice that the first step has already been done in the previous section. The maximum information entropy after the first step is given by the Sackur-Tetrode expression (22). In the second step we have to find the ensemble temperature that makes the information entropy (22) with the constraint that

$$\mathcal{E}_{\text{kin}} = \frac{3}{2} \int d\mathbf{r} n(\mathbf{r}) kT(\mathbf{r}). \quad (29)$$

That is,

$$S = -k \int d\mathbf{r} n(\mathbf{r}) \ln n(\mathbf{r}) + \frac{1}{2} k \int d\mathbf{r} n(\mathbf{r}) [3 \ln (2\pi mkT) + 5] + \zeta \left(\mathcal{E}_{\text{kin}} - \frac{3}{2} \int d\mathbf{r} n(\mathbf{r}) kT(\mathbf{r}) \right), \quad (30)$$

where ζ is the Lagrange multiplier. Note that the orbitals and the density are kept fixed. The variation leads to

$$\frac{3}{2} \frac{kn}{T} - \zeta \frac{3}{2} kn = 0. \quad (31)$$

Therefore,

$$\frac{1}{T} = \zeta. \quad (32)$$

As the Lagrange multiplier ζ is a constant, the temperature T of the ensemble is also a constant. It has the consequence that according to Eq.(18) the ensemble non-interacting kinetic energy density is proportional to the ensemble density n . Eqs.(27) and (28) lead to

$$T = \frac{2}{3} \frac{E_{\text{kin}}}{kN}. \quad (33)$$

The distribution function obtained by the constrained search is a Maxwell-Boltzmann distribution function

$$f(\mathbf{r}, \mathbf{p}) = [2\pi mkT]^{-3/2} n(\mathbf{r}) e^{-p^2/2mkT}, \quad (34)$$

that is, Eq.(21) with the constant ensemble temperature (33).

5 Discussion and illustrative examples

Take the linear harmonic oscillator as the first the example. The potential is $V = \frac{1}{2} m\omega^2 x^2$, where m is the mass and ω is the frequency. The eigenvalues are

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right), \quad (35)$$

where $n = 0, 1, \dots$ is the quantum number. Because of the virial theorem the kinetic energies are

$$E_{\text{kin}}^n = \frac{1}{2} \hbar\omega \left(n + \frac{1}{2} \right). \quad (36)$$

The ensemble kinetic energy is

$$\mathcal{E}_{\text{kin}} = \sum_{n=1}^M w_n E_{\text{kin}}^n = \frac{1}{2} \hbar\omega \left(\sum_n n w_n + \frac{1}{2} \right). \quad (37)$$

Consequently the ensemble temperature is

$$T = \frac{1}{k\beta} = \frac{\hbar\omega}{k} \left(\sum_n n w_n + \frac{1}{2} \right). \quad (38)$$

In the subspace theory of Theophilou⁴ $w_1 = \dots = w_M = 1/M$, the ensemble kinetic energy and the ensemble temperature take the form

$$\mathcal{E}_{\text{kin}} = \frac{M\hbar\omega}{2} \quad (39)$$

and

$$T = \frac{1}{k\beta} = \frac{M\hbar\omega}{2k}, \quad (40)$$

respectively.

Our second example is the hydrogen atom. The eigenvalues are

$$E_n = -\frac{1}{2} \frac{Z^2}{n^2} a_0 = -E_{\text{kin}}^n, \quad (41)$$

where

$$a_0 = \frac{\hbar^2}{me^2}. \quad (42)$$

Z , m and e and $n = 1, 2, \dots$ are the atomic number, the electron mass, the magnitude of the electronic charge and the principal quantum number, respectively. In the second equality of Eq.(41) the virial theorem was used. Then, the ensemble kinetic energy is

$$\mathcal{E}_{\text{kin}} = \frac{1}{2} \sum_{i=1}^K w_i \frac{Z^2}{n_i^2} a_0, \quad (43)$$

where K is the number of different principal quantum numbers n . In the subspace theory of Theophilou we have

$$w_i = \frac{n_i^2}{M}, \quad (44)$$

where we make use of the fact that the degeneracy of a level with the principal quantum number n is n^2 . Therefore the ensemble kinetic energy and the ensemble temperature have the form

$$\mathcal{E}_{\text{kin}} = \frac{1}{2} Z^2 \frac{K}{M} a_0 \quad (45)$$

and

$$T = \frac{1}{3} Z^2 \frac{K}{kM} a_0, \quad (46)$$

respectively.

One of our interesting results is that the ensemble temperature corresponding to the extremum phase-space information entropy is constant. This is true for any ensemble irrespective of the construction of the ensemble, that is, the weighting factors. Of course, the ensemble kinetic energy and consequently, the ensemble temperature will depend on the weighting factors, but it will always be a constant.

The ensemble kinetic energy density maximizing the phase-space information entropy is found to be proportional to the ensemble density. We emphasize here, that the knowledge of the ensemble kinetic energy density does not give us any information about the ensemble kinetic energy functional or its functional derivative.

This paper emphasizes the non-uniqueness of the local thermodynamics and shows that the maximum entropy is attained if the ensemble temperature is constant. The ambiguity of the local thermodynamics can also be considered an advantage from the point of view of practical applications. One is free to select that particular ensemble local temperature (or ensemble kinetic energy density) that is the most suitable for the given application. It might happen that the constant ensemble temperature is the most favorable in certain cases. In other cases, another ensemble kinetic energy density and the corresponding temperature are more beneficial. It means that they can provide different physical or chemical insight.

From information theoretic viewpoint the present theory has the significance that it is possible to select an ensemble kinetic energy density that is proportional to the ensemble density. It means that the ensemble kinetic energy density has almost the

same information as the ensemble density. There is a difference only in the normalization: the ensemble density integrates to the number of electrons, while the ensemble kinetic energy density is normalized to the ensemble kinetic energy. That is, the maximum entropy is attained by the ensemble kinetic energy density having no new information in addition to the ensemble density.

6 Conclusions

In summary, we constructed ensembles of excited states and selected that ensemble kinetic energy density that maximizes the phase-space information entropy. The extremum was obtained through the constrained search of Levy and Lieb. This ensemble kinetic energy density is proportional to the ensemble density and the ensemble temperature is constant.

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