Local thermodynamical formalism for ensembles of excited states

Á Nagy
Department of Theoretical Physics, University of Debrecen, Debrecen, Hungary
Email: anagy@phys.unideb.hu
Received 28 March 2014; revised and accepted 7 April 2014

The thermodynamical formalism of density functional theory is generalized for ensembles of excited states. Ensemble local temperature is defined. A family of novel descriptors of Coulomb systems is introduced.

Keywords: Theoretical chemistry, Density functional calculations, Excited states

It started with a 1984 paper by Ghosh, Berkowitz and Parr entitled "Transcription of ground-state density functional theory into a local thermodynamics". They provided a statistical foundation emphasizing that the kinetic energy varies from point to point and therefore local thermodynamical quantities, such as temperature, free energy, and entropy are defined. Later the local temperature proved to be a quantitative indicator of chemical reactivity.

An 'exact' thermodynamics beyond the GBP theory was developed by Nagy and Parr. A general "local density" version of the theory was described, and the GBP theory recovered as a special case. The same Sackur-Tetrode expression was derived for the local entropy, earlier obtained by other methods, incorporating corrections in this equation for "nonideality". It was found that the thermodynamical entropy measures (up to a constant) the deviation from the Thomas-Fermi model. The formalism leads to an alternative proof of Teller's theorem. The thermodynamical entropy measures the wave function quality provided that a particularly preferred definition of the local kinetic energy density is implied.

The density functional theory has also been extended for ensembles of unequally weighted states by Oliveira, Gross and Kohn. (For reviews of excited-state theory, see Refs 13 & 14).

Approximations are important not only in the ground-state but also in the ensemble state theories, because the exact form of the exchange-correlation energy functional is unknown in both the theories. The quasi-local-density approximation of Kohn was followed by the application of ground-state functionals. Then, the optimized potential method (OPM) and the Krieger-Li-Iafrate (KLI) method were also extended to ensembles of excited states. The relativistic generalization of ensemble formalism was also done. The adiabatic connection formula for the ensemble exchange-correlation energy and the virial theorem were also derived in the ensemble theory. The concept of the ensemble Kohn-Sham hardness was introduced as a reactivity index. As an interesting example of the ensemble theory, two harmonically interacting electrons with antiparallel spins under isotropic harmonic confinement was studied.

In this paper the local thermodynamical formalism is extended to ensembles of excited states. In the following section, the ensemble theory of excited states is summarised. Then the local thermodynamical formalism is introduced for ensembles. Thereafter, a family of novel descriptors of Coulomb systems is introduced. Finally, the last section is devoted to an example and discussion.
Ensembles of Excited States in Density Functional Theory

Consider the eigenvalue problem of the Hamiltonian,
\[ \hat{H} \psi_k = E_k \psi_k \quad (k = 1, \ldots, M) \quad \cdots (1) \]
where
\[ E_1 \leq E_2 \leq \ldots \leq E_M \quad \cdots (2) \]
The ensemble energy and density are defined as Eqs (3) and (4) respectively,
\[ E = \sum_{k=1}^{M} w_k E_k \quad \cdots (3) \]
\[ n = \sum_{k=1}^{M} w_k n_k \quad \cdots (4) \]
where \( n_k \) is the electron density obtained from the wave function \( \psi_k \) and
\[ 0 \leq w_M \ldots \leq w_2 \leq w_1 \quad \cdots (5) \]

Generalized Hohenberg-Kohn theorems were derived for the ensembles. The ensemble density determines the external potential within a trivial additive constant. A generalization of the Rayleigh-Ritz variational principle was proved to be valid for the ensemble energy \[ \cdots (6) \]
\[ (-\frac{1}{2} \nabla^2 + v_{KS}) u_i = \epsilon_i u_i \quad \cdots (6) \]
where \( u_i \), \( \epsilon_i \) and \( v_{KS} \) are the ensemble orbitals, energies and Kohn-Sham potential, respectively. The ensemble density can be expressed with the orbitals as Eq. (7),
\[ n = \sum_{i=1}^{K} \lambda_i |u_i|^2 \quad \cdots (7) \]
where the occupation numbers \( \lambda_i \) are not all integer. \( K \) denotes the number of orbitals with non-zero occupation numbers. The non-interacting ensemble kinetic energy can also be expressed with the ensemble orbitals as Eq. (18),
\[ E_{kin} = \sum_{i=1}^{K} \lambda_i \int u_i (-\frac{1}{2} \nabla^2) u_i \quad \cdots (8) \]

Local Thermodynamical Formalism For Ensembles of Excited States

Now, the theory of Ghosh, Berkowitz and Parr is generalized for ensembles. Consider a system of \( N \) electrons moving in a local external potential. The ensemble is characterized by a distribution function \( f(r, p) \) in the phase space satisfying the properties,
\[ \int dp \, f(r, p) = n(r) \quad \cdots (9) \]
\[ \int dr \, n(r) = N \quad \cdots (10) \]

and
\[ \int dp \, f(r, p) \frac{p^2}{2} = t_s(r) \quad \cdots (11) \]
where the ensemble non-interacting kinetic energy density \( t_s(r) \) integrates to the ensemble non-interacting kinetic energy \( E_{kin} \) (Eq. 12),
\[ \int dr \, t_s(r) = E_{kin} \quad \cdots (12) \]

The distribution function can be obtained by the criterion of maximum entropy. The ensemble entropy (Eq. 13),
\[ S = \int dr \rho_s(r) \quad \cdots (13) \]
is maximized subject to the constraints of correct ensemble density (Eq. 9) and correct ensemble kinetic energy density (Eq. 11). The ensemble entropy density is given by Eq. 14,
\[ \rho_s(r) = -k \int dp \, f(\ln f - 1) \quad \cdots (14) \]
where \( k \) is the Boltzmann constant. Then the ensemble distribution function takes the form of Eq. 15,
\[ f(r, p) = e^{-\alpha(r)-\beta(r)p^2/2} \quad \cdots (15) \]
where \( \alpha(r) \) and \( \beta(r) \) are \( r \)-dependent Lagrange multipliers. The ensemble local temperature \( T(r) \) is introduced via the ensemble non-interacting kinetic energy density (Eq. 16),
\[ t_s(r) = \frac{3}{2} n(r) kT(r) \quad \cdots (16) \]

As the ensemble non-interacting system is utilized, it is natural to apply an ideal gas-like expression (Eq. 16). The ensemble distribution function can be rewritten as Eq. 17,
\[ f(r, p) = [2\pi kT(r)]^{-3/2} n(r) e^{-p^2/(2kT(r))} \quad \cdots (17) \]
where
\[
\beta(r) = \frac{1}{kT(r)}.
\]

It should be emphasized that the kinetic energy density is not unique. One can use several forms, all of which lead to the same kinetic energy. Here the gradient form is selected (Eq. 19),
\[
t_s = \frac{1}{\mathbf{r}} \sum_{i=1}^{K} \lambda_i \frac{\nabla n_i \cdot \nabla n_i}{n_i}.
\]

where \(n_i = |\psi_i|^2\) is the one-particle density. It has the advantage of being non-negative, and therefore the local temperature is nowhere negative (See Eq. 19). In the vicinity of an atomic nucleus, the ensemble density is close to \(n_{1s}\). Therefore,
\[
\frac{3}{2} kT(r) \approx \frac{1}{2} Z^2 \quad \text{(near an atomic nucleus)} \quad \ldots (20)
\]

Far from all nuclei, the ensemble density is mainly the highest occupied orbital density of the ensemble, \(n \sim \exp(-2r/\sqrt{2|\epsilon_K|})\), where \(\epsilon_K\) is the highest occupied one-electron density in the ensemble. \((\epsilon_K = -l\), where \(l\) is the ionization energy of the highest excited state in the ensemble. \(l\) can be considered as the ensemble ionization energy).
\[
\frac{3}{2} kT(r) \approx -\epsilon_K = l \quad \text{(far from all nuclei)} \quad \ldots (21)
\]

Substituting the ensemble distribution function (Eq. 17) into the ensemble entropy expression (Eq. 14), we obtain Eq. (22).
\[
\rho_s(r) = -kn \ln n + \frac{3}{2} kT \ln T + \frac{1}{2} kT [5 + 3 \ln (2\pi n)]
\]

\[
\ldots (22)
\]

**Novel Descriptors of Coulomb Systems**

Earlier a family of descriptors of Coulomb systems was introduced. Now a generalization for ensembles is presented. Consider the expression,
\[
\xi(r) = \sum_{i=1}^{K} \theta_i n_i,
\]

where \(\theta_i \geq 0\) for \(1 \leq i \leq K\) and \(\theta_K > 0\).

**Theorem 1.** For any Coulomb system, \(\xi(r)\) determines the external potential \(v(r)\) up to an additive constant and the number of electrons.

**Proof:** The external potential in a Coulomb system is given by Eq. (24).
\[
v(r) = -\sum_{\beta} \frac{Z_\beta}{|r-R_\beta|}.
\]

The atomic number \((Z_\beta)\) of the nucleus at the position \(R_\beta\) can be determined from the cusp condition derived in earlier papers. Consider the function \(\eta_l\).
\[
\eta_l = \frac{n_{l\beta}(r)}{r^{2l}} \quad \ldots (25)
\]

where \(n_{l\beta}(r)\) is the spherical average of the orbital density, \(n_{l\beta}\) around the nucleus, \(\beta\), \(l\) is the smallest integer for which \(\eta_l\) is not zero at the nucleus \(\beta\). We earlier proved the cusp relationship.
\[
\eta_l'(R_\beta) = -2Z_\beta \frac{\theta_\beta}{l+1} \eta_l(R_\beta) \quad \ldots (26)
\]

This relationship reduces to the well-known form, \(\eta_l'(R_\beta) = -2Z_\beta \xi(R_\beta)\) if \(l = 0\). The function is now defined as
\[
\eta_l = \frac{\xi(r)}{r^{2l}} \quad \ldots (27)
\]

The cusp relation has the form
\[
\eta_l'(R_\beta) = -2Z_\beta \frac{\theta_\beta}{l+1} \eta_l(R_\beta) \quad \ldots (28)
\]

at the nucleus \(\beta\). This relation reduces to \(\xi'(R_\beta) = -2Z_\beta \xi(R_\beta)\) if \(l = 0\), that is, the factor \(\theta\) is larger than zero for at least one of the \(s\) orbitals. Thus, the cusp relationship gives the atomic numbers and the position of the nuclei.

We can also prove that \(\xi\) determines the number of electrons. It is a consequence of the fact that the asymptotic decay of \(\xi\) is given by the highest occupied orbital (Eq. 29),
\[
\xi(r \to \infty) \sim n_{K\beta}(r \to \infty) \sim r^{-2/4} \left(\frac{Z_{tot}-N+1}{\sqrt{2|\epsilon_{K\beta}|}}\right) e^{-2r/\sqrt{2|\epsilon_{K\beta}|}} \quad \ldots (29)
\]

where \(Z_{tot}\) is the sum of the atomic numbers. Therefore, the number of electrons can be determined by Eq. (30).
\[
N = 1 + \left[ Z_{tot} + \frac{1}{4} \lim_{r \to \infty} \left( \frac{\partial \ln \xi}{\partial r} \left(\frac{\partial^2 \ln \xi}{\partial r^2} \right) + 2 \right) \right] \quad \ldots (30)
\]

There are several interesting special cases:
If \(\theta_i = \lambda_i\) are the occupation numbers \((1 \leq i \leq K)\), the ensemble density is recovered: \(\xi(r) = n(r)\). If \(\theta_i = \lambda_i / N\) with \((1 \leq i \leq K)\), the ensemble shape function is recovered: \(\xi(r) = \sigma(r) = n(r)/N\).
If \( \theta_i = \lambda_i^1 \) are the ground-state occupation numbers 
\( (1 \leq i \leq N) \), the ground-state density is recovered: 
\[ \xi(r) = n_1(r). \]
If \( \theta_i = \lambda_i^k \) are the \( k \)th excited-state occupation numbers, the \( k \)th excited-state density is recovered: 
\[ \xi(r) = n_k(r). \]
If \( \theta_1 = \ldots = \theta_{N-1} = 0 \) and \( \theta_N = 1 \), \( \xi \) is the highest occupied ground-state orbital density.
If \( \theta_1 = \ldots = \theta_{K-1} = 0 \) and \( \theta_K = 1 \), \( \xi \) is the highest occupied \( k \)th excited-state orbital density.

**Illustration and Discussion**

As an illustration consider hydrogen-like ions. The ground-state density has the form 
\[ n_1(r) = \frac{Z^2}{\pi} e^{-2Zr} \] 
where \( Z \) is the atomic number (Atomic units are used). The first excited-state is degenerate. Both the 2s and 2p states have to be considered to construct the ensemble density 
\[ n_2(r) = \frac{Z^2}{8\pi} \left[ \left(1 - \frac{Zr}{2}\right)^2 + \frac{(Zr)^2}{4} \right] e^{-Zr} \]

The non-interacting kinetic energy densities of the ground and first excited states are given by Eqs (33) and (34), respectively.

\[ t_1(r) = \frac{Z^2}{2\pi} e^{-2Zr} \] 

and

\[ t_2(r) = \frac{Z^2}{16\pi} \left[ \left(1 - \frac{Zr}{4}\right)^2 + \frac{Z^2}{2} \left(3 - Zr + \frac{(Zr)^2}{4}\right) \right] e^{-Zr} \]

Now, consider the ensemble constructed from the ground and the first excited states: \( n_w = w_1n_1 + w_2n_2 \), where \( w_1 = 1 - 4w \) and \( w_2 = 4w \), taking into account the degeneracy of the states. Then the ensemble density has the form 
\[ n_w(r) = \frac{Z^3}{\pi} \left\{ e^{-2Zr} + w \left[ 1 - Zr + \frac{(Zr)^2}{2} \right] e^{-Zr} - 4e^{-2Zr} \right\} \]

The ensemble kinetic energy density can be written as 
\[ t_w(r) = \frac{Z^5}{2\pi} \left\{ e^{-2Zr} + w \left[ 1 + \frac{3}{4} \left( Zr + \frac{(Zr)^2}{2} \right) e^{-Zr} - 4e^{-2Zr} \right] \right\} \]

The ensemble local temperature is 
\[ T_w(r) = \frac{Z^2}{3k} \left[ 1 + w \left[ 1 - Zr + \frac{(Zr)^2}{2} \right] e^{Zr} - 4 \right] \]

Figure 1 presents \( \frac{kT}{Z^2} \) as a function of \( Zr \) for the weighting factors 0, 0.1 and 0.2. The minimal value of the weighting factor is 0, while the maximal value is 0.2. The case \( w = 0 \) corresponds to the ground state, where \( \frac{kT}{Z^2} = \frac{1}{3} \) is a constant. For other values of \( w \), that is, for an ensemble, there is an \( r \)-dependence in the local temperature. From Eq. (37) we can see that \( \frac{kT}{Z^2} \) takes the value of 1/12 for \( r \to \infty \) for any value of \( w \) except 0. We can also observe that the curves meet at \( Zr = \frac{1}{3} \left(1 + \sqrt{19}\right) \approx 1.786 \). This result can be easily verified using the expression of the ensemble local temperature.

The ensemble Kohn-Sham equations have the same form as the ground-state Kohn-Sham equations. (The ensemble Kohn-Sham orbitals, energies and the Kohn-Sham potential are, of course, different). The consequence of this similarity is that the local ensemble thermodynamics has the same structure as the ground-state. One can define the local ensemble entropy, temperature and other quantities in the same...
way as in the ground state. The ensemble expressions have the same form as in the ground state. The difference is in the fact that the ensemble density and kinetic energy density are different from the ground-state ones.

The exact form of the ensemble exchange-correlation functional is not known as it is unknown in the ground state. We also have to keep in mind that the ensemble depends on the weighting factors. In principle, any choice of the weighting factors satisfying inequality (Eq. 5) is appropriate. However, in practice, different weighting factors might lead to different results as approximate functionals have to be applied in the calculations.

In the ground-state theory, the local temperature proved to be a quantitative indicator of chemical reactivity; molecular sites with high reactivity towards electrophiles have low local temperature. Double and triple bonds in small molecules can be distinguished by the behavior of the local temperature. The applicability of the ensemble temperature in chemical reactivity will be the subject of further research. The ensemble local and differential virial theorems derived recently are closely related to the thermodynamical formalism.

Both the ground-state and the ensemble densities are fundamental quantities. They determine every property of an electron system. In the special case of Coulomb systems there are several other descriptors that also contain all information about the system. Such reactivity indicators are the shape function, the Fukui function, local softness, softness kernel, local kinetic energy and the electrostatic potential. Here a broader family of quantities, which are all capable of fully determining every property of a Coulomb system, are presented. This family contains several of the previously known quantities and a large number of new ones. These novel descriptors are related to ensemble and excited state energies and are anticipated to be good reactivity indices.

Acknowledgement

The work was supported by the TAMOP 4.2.2.A-11/1/KONV-2012-0036 project. The project was co-financed by the European Union and the European Social Fund. Grant OTKA No. K 100590 is also gratefully acknowledged.

References