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Chemical potential inequality principle*

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Abstract. Regional density functional theory has been extended to treat irreversible thermodynamic electronic processes for application to adiabatic electron-transfer processes of chemical reactions. Onsager's local equilibrium hypothesis is slightly modified to take into account the quantum mechanical nature of the electron. The quantum mechanical interference effect has been demonstrated to be included in the entropy production rate formula associated with electron transfer through an interface. A new formula for the determination of the transition state of a chemical reaction has been postulated that corresponds to the maximum of the regional electron transferability. A quantum mechanical law of mass action has been established and applied to prove the regional electrochemical potential inequality principle.

Key words: Chemical potential inequality principle – Regional density functional theory – Irreversible thermodynamics – Interface – Quantum mechanical law of mass action

1 Introduction

Gibbs proved the usefulness of the constant chemical potential between two regions in space where we observe no flux of particles whatsoever when chemical equilibrium is attained globally [1]. The constancy of the chemical potential is perturbed if we put an object between a pair of regions, when the transfer of particles is rather inhibited through the interface, bringing about a finite difference in regional chemical potentials even after chemical equilibrium is attained globally [2]. The object may in some cases be represented as a semipermeable membrane. If the particles are electrons, quantum mechanical tunneling is allowed through the barrier of the interface, and the common value of the chemical potential acquires physical reality as the Fermi level, a well-defined useful quantity. For electrons, however, the regional energies are not free from the long-range Coulomb interactions nor the off-diagonal matrix elements that should act even through the interface. Although screening effects may somehow hide the long-range Coulomb interactions, the off-diagonal terms in the density matrix should still play an important role that is representative of the nonlocal coherent nature of the electronic wave function, the very nature of the quantum mechanics of electrons. The consequence is that there remain finite differences in the regional chemical potentials even though the Fermi level is defined rigorously following the condition of the global equilibrium; this inhomogeneity of regional chemical potentials was proved in an earlier paper using the complementary regions P and Q that span the whole space [3–5], and the proof is here referred to as the regional electrochemical potential inequality principle or the chemical potential inequality principle for short.

It is the aim of this article to demonstrate the chemical potential inequality principle in a more general situation where we start from the treatment of irreversible electronic processes over more than two regions in a chemical reaction system under external perturbations.

Let us consider a chemical reaction system A embedded in a medium M, an environmental system of chemical reaction. During the progress of chemical reaction in A, the electronic subsystem of A can exchange heat, work, and electrons with M through an interface which divides A from M. Moreover, the electronic subsystem of A can exert work on the nuclear subsystem of A, and vice versa, where the nuclear subsystem of A is assumed to be thermally isolated from the medium M as well as from the electronic subsystem of A. This is the adiabatic approximation that we rely on throughout in this article, and we neglect relativistic effects as well. If the electronic subsystem of A is in chemical equilibrium with the medium M and the chemical reaction in A is a quasi-static process, then the maximum work is gained

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from the electronic subsystem of A, and therefore only the minimum work is required for the nuclear subsystem of A [1], where the pathway of the nuclear configuration change is given by using the theory of the intrinsic reaction coordinate (IRC) or meta-IRC [6, 7].

The adiabatic electron transfer in the chemical reaction system A is studied by regional density functional theory [3–5], in which we have assumed that at every moment of fixed configuration for the nuclear subsystem of A the electrons are redistributed in A with no excess or loss adapted to each region of space, whereby any irreversible electron flow which may be brought about by the infinitesimal successive change of nuclear configuration should ultimately disappear; this is quite a natural assumption. Even in the absence of M, the distribution of the electronic density $\rho(r)$ in the electronic subsystem of A is inhomogeneous, reflecting the inhomogeneous discrete distribution of nuclei in A. However inhomogeneous $\rho(r)$ should be, Mermin [8] proved that the thermodynamic potential Ω for the electronic subsystem of A is a unique function of $\rho(r)$:

$$\Omega[\rho] = Tr\hat{\rho}[\rho]\left[\hat{H} - \mu_G\hat{N} + \frac{1}{\beta}\ln(\hat{\rho}[\rho])\right] \ , \tag{1}$$

$$= E[\rho] - \mu_G N[\rho] - TS[\rho] \ , \tag{2}$$

$$E[\rho] = F[\rho] + \int dr\, \rho(r)v(r) \ , \tag{3}$$

where $\hat{\rho}$, $\hat{H}$, $\hat{N}$, E, N, S, T, μ_G, β, F, and $v(r)$ denote the density matrix, the electronic Hamiltonian, the electron number operator, the electronic energy, the electron number, the electronic entropy, the absolute temperature, the Gibbs electrochemical potential or the Gibbs chemical potential for short, the inverse temperature, the universal functional, and the external potential composed of electron-nuclear Coulomb attraction energies, respectively. The Gibbs chemical potential μ_G is obtained as

$$\mu_G = \left(\frac{\partial E}{\partial N}\right)_{S,v} \ , \tag{4}$$

which is the change in the electronic energy E as a function of the electron number N.

In harmony with the inhomogeneity of $\rho(r)$, we have given a mathematical proof of the inhomogeneity of the regional chemical potentials [3–5]. Indeed, in terms of the complementary regions P and Q that span the whole space, we have

$$\mu_P \neq \mu_Q \ , \tag{5}$$

where μ_P and μ_Q denote the regional chemical potentials

$$\mu_P = \left(\frac{\partial E_P}{\partial N_P}\right)_{S,N_Q,v} , \quad \mu_Q = \left(\frac{\partial E_Q}{\partial N_Q}\right)_{S,N_P,v} \ , \tag{6}$$

with regional electronic energies $E_{P,Q}$ and electron numbers $N_{P,Q}$ that satisfy

$$E = E_P + E_Q \ , \tag{7}$$

$$N = N_P + N_Q \ . \tag{8}$$

The difference in Eq. (5) has been given as

$$\mu_P - \mu_Q = \tau_P - \tau_Q \quad \text{(difference rule)} \ , \tag{9}$$

where $\tau_{P,Q}$ denotes the regional transfer potentials defined as

$$\tau_P = \left(\frac{\partial E_P}{\partial N}\right)_{S,v,\Gamma} , \quad \tau_Q = \left(\frac{\partial E_Q}{\partial N}\right)_{S,v,\Gamma} \ , \tag{10}$$

which are summed up to give μ_G,

$$\mu_G = \tau_P + \tau_Q \quad \text{(sum rule)} \ , \tag{11}$$

where the subscript Γ in Eq. (10) denotes the coordinate of electron transfer [3]. The chemical potential inequality principle is schematically shown in Fig. 1.

It is not, however, a trivial matter to "observe" the inhomogeneity of the regional chemical potentials using appropriate apparatus. A promising candidate for this kind of measurement may be found in a study of the work function of metals as a function of crystallographic planes [9]. The medium M in this measurement of the work function is used to observe the electrostatic potential energy of an electron at a point in the neighborhood of the crystal surface plane just outside of it [10], where a clever choice of apparatus could allow the chemical potential inequality principle to be proved. However, we are not in a position here in this article to invent a device if the medium M is situated in such a way as to discriminate against the regional chemical potentials. Rather, we shall devise a method to probe the transfer of electrons within the electronic subsystem of A from one region to another through the interface situated in-between. The subdivision of the electronic subsystem of A into regions R, R′, R″, and so on is shown schematically in Fig. 2a. In a region, R say, the electronic subsystem of A is assumed to be in chemical equilibrium, but we allow irreversible electron flow through the interface that divides R and the adjacent region, R′ say.

This situation is nothing but the local equilibrium hypothesis due to Onsager [11, 12] and is adapted in this article in order to treat irreversible electron transfer in the electronic subsystem of A. In the irreversible thermodynamics of Onsager, there is a gradient of chemical potentials, where Eq. (5) is mandatory. We shall slightly modify the theory of Onsager in such a way that the

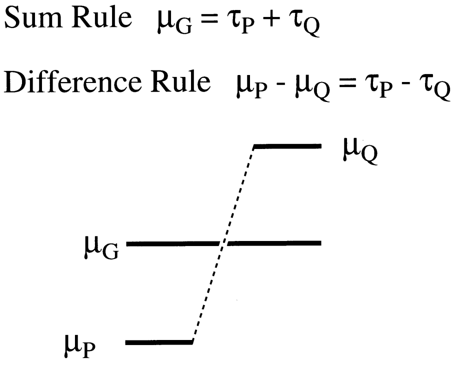
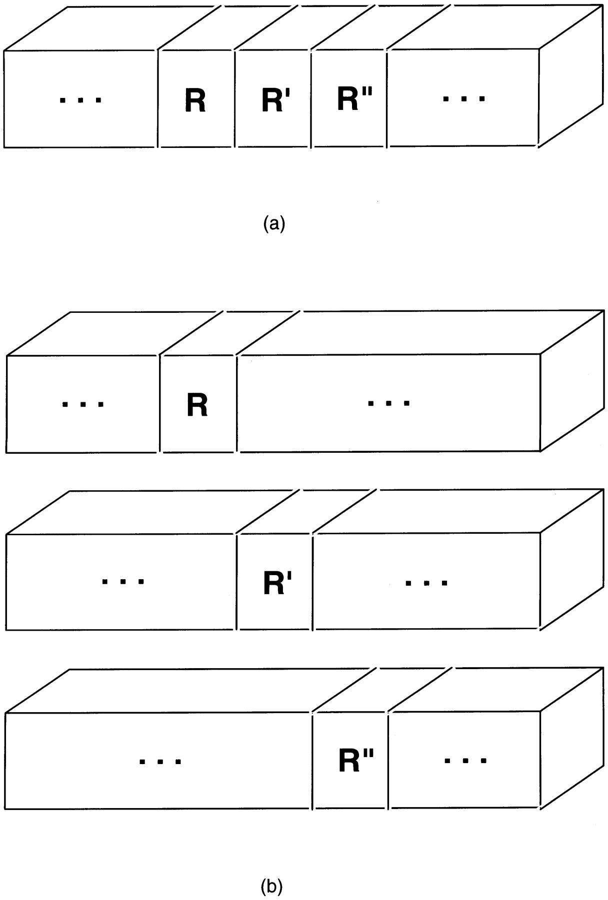


Fig. 1. The chemical potential inequality principle



(a)

(b)

Fig. 2. Regional partitioning: **a** interface structure, and **b** Onsager's hypothesis of local equilibrium

quantum mechanical interference effect works through the interfaces that divide the regions in the electronic subsystem of A. This quantum mechanical interference effect survives even in the limit of global chemical equilibrium, leading to the chemical potential inequality principle that predicts the inequality in-between either

1. The Gibbs chemical potential μ_G for the electronic subsystem of A as a whole and the regional chemical potential μ_R, or
2. The regional chemical potentials μ_R themselves.

Unless otherwise stated explicitly, we do not use the zero-temperature limit in each equation, as was implicitly performed in our preceding papers [3–5].

2 Extension of Onsager's local equilibrium theory

2.1 Local equilibrium under quantum mechanical interference effects

In his original theory, Onsager established a local equilibrium hypothesis in the treatment of irreversible thermodynamic processes. According to his hypothesis, we need the number of the Gibbs ensembles which is as many as the number of regions as shown in Fig. 2b. In his original hypothesis, each region has its own Hamiltonian; however, we shall now allow the quantum mechanical coherency of electrons that can tunnel to neighboring regions surrounding the region R of interest. This slight extension can be performed using apparatus density functional theory where we need only one electronic Hamiltonian that covers the system as a whole and the distribution of electron density that possesses coherency is treated as the apparatus for the region R of interest [3]. Thus we get the density matrix

$$\hat{\rho}* = \exp(-\beta_R \hat{H} - \gamma_R \hat{N}) / Tr \exp(-\beta_R \hat{H} - \gamma_R \hat{N}) \tag{12}$$

with

$$\hat{H} = \hat{H}_A - \sum_i \lambda_{iR} \hat{A}_{iR} - \int dr\, v_R(r) \hat{N}(r) \ , \tag{13}$$

where $\hat{H}_A$, $\hat{A}_{iR}$, and $\hat{N}(r)$ denote, respectively, the Hamiltonian of the system A, the apparatus operator, and the electron density operator. The electron density operator $\hat{N}(r)$ is integrated to give the electron number operator $\hat{N}$,

$$\hat{N} = \int dr\, \hat{N}(r) \ . \tag{14}$$

The Lagrange multipliers in $\hat{\rho}*$ are

1. The inverse temperature β_R,

$$\beta_R = \frac{1}{k_B T_R} \tag{15}$$

with the temperature T_R and the Boltzmann constant k_B.

2. The Gibbs chemical potential μ_{GR},

$$\gamma_R = -\beta_R \mu_{GR} \ . \tag{16}$$

3. The apparatus parameter λ_{iR}.
4. The controlling function $v_R(r)$ of electron density.

The Hamiltonian $\hat{H}$ reduces to the original Hamiltonian $\hat{H}_A$ of the electronic subsystem A when we treat the equilibrium state in the absence of apparatuses.

Since we are treating local equilibrium under the presence of apparatuses, the Mermin entropy principle ensures the maximum entropy using $\hat{\rho}*$ in Eq. (12)

$$S = -k_B Tr \hat{\rho}* \ln \hat{\rho}* = \text{maximum} \ . \tag{17}$$

By assuming that we use a nonrelativistic Hamiltonian, the apparatus should not absorb or create electrons, and hence $\hat{H}$ as well as $\hat{H}_A$ should be commutable with $\hat{N}$,

$$[\hat{H}, \hat{N}] = 0 \ , \tag{18}$$

so that $\hat{H}$ and $\hat{N}$ are simultaneously diagonalized to give

$$\hat{H} |j\rangle = E_j |j\rangle \ , \tag{19}$$

$$\hat{N} |j\rangle = N_j |j\rangle \ , \tag{20}$$

and therefore

$$\hat{\rho}* = \sum_j |j\rangle p_j \langle j| \tag{21}$$

$$p_j = \exp(-\beta_R E_j - \gamma_R N_j) \Xi_R \ , \tag{22}$$

where we have used the partition function

$$\Xi_{\mathrm{R}} = \sum_{j} \exp(-\beta_{\mathrm{R}} E_j - \gamma_{\mathrm{R}} N_j) \ , \tag{23}$$

and the normalization condition

$$Tr|j\rangle\,\langle j| = 1 \ . \tag{24}$$

The total electronic energy E and the total electron number N are given by

$$E = Tr\hat{\rho}*\hat{H} = \sum_{j} p_j E_j \ , \tag{25}$$

$$N = Tr\hat{\rho}*\hat{N} = \sum_{j} p_j N_j \ . \tag{26}$$

It should be noted that the electron density $\rho_j(r)$ for the state j is obtained as the diagonal part of the first-order reduced density matrix and satisfies

$$\int dr\rho_j(r) = N_j Tr|j\rangle\,\langle j| = N_j \ . \tag{27}$$

In other words, the normalization condition, Eq. (24), reads

$$Tr|j\rangle\,\langle j| = \frac{\int dr\rho_j(r)}{N_j} = 1 \ . \tag{28}$$

2.2 Regional partitioning

In a previous study, we introduced a device to calculate regional quantities using reduced density matrices [3, 4]. The manipulation is based on the coordinate representation of the density matrix, where the multiple integration with respect to spatial Cartesian coordinates r_i and spin coordinates σ_i for the ith electron is divided into

$$\int \prod_{i} dr_i\, d\sigma_i = \int dr_1 \int d\sigma_1 \prod_{i(\neq 1)} dr_i\, d\sigma_i \ , \tag{29}$$

and the final integration is further divided into a regional partitioned form

$$\int dr_1 = \sum_{\mathrm{R}} \int_{\mathrm{R}} dr_1 \ , \tag{30}$$

where the subscript R of the integration symbol dictates integration confined solely to the particular region R.

In particular, for example, the electron number N_j of the jth state is partitioned into a regional electron number $N_{j\mathrm{R}}$ as follows

$$N_j = \int dr\rho_j(r) = \sum_{\mathrm{R}} N_{j\mathrm{R}}, \quad N_{j\mathrm{R}} = \int_{\mathrm{R}} dr\rho_j(r) \ , \tag{31}$$

where we have used Eqs. (27) and (30). In other words, using Eqs. (28), (30), and (31), we have

$$Tr|j\rangle\,\langle j| = \sum_{\mathrm{R}} \omega_{j\mathrm{R}} = 1, \quad \omega_{jR} = \frac{N_{j\mathrm{R}}}{N_j} \ . \tag{32}$$

Hence, we obtain the following regional partitionings:

$$E_j = \sum_{\mathrm{R}} E_{j\mathrm{R}}, \quad E_{j\mathrm{R}} = E_j \omega_{j\mathrm{R}} \ , \tag{33}$$

$$N_j = \sum_{\mathrm{R}} N_{j\mathrm{R}}, \quad N_{j\mathrm{R}} = N_j \omega_{j\mathrm{R}} \ , \tag{34}$$

$$\rho_j(r) = \sum_{\mathrm{R}} \rho_{j\mathrm{R}}(r), \quad \rho_{j\mathrm{R}}(r) = \rho_j(r) \text{ in R}, = 0 \text{ otherwise} \ . \tag{35}$$

Analogously, we obtain

$$E = \sum_{\mathrm{R}} E_{\mathrm{R}}, \quad E_{\mathrm{R}} = \sum_{j} p_j E_{j\mathrm{R}} = \sum_{j} p_j E_j \omega_{j\mathrm{R}} \ , \tag{36}$$

$$N = \sum_{\mathrm{R}} N_{\mathrm{R}}, \quad N_{\mathrm{R}} = \sum_{j} p_j N_{j\mathrm{R}} = \sum_{j} p_j N_j \omega_{j\mathrm{R}} \ , \tag{37}$$

$$\rho(r) = \sum_{\mathrm{R}} \rho_{\mathrm{R}}(r), \quad \rho_{\mathrm{R}}(r) = \sum_{j} p_j \rho_{j\mathrm{R}}(r) \ . \tag{38}$$

Moreover, Eq. (17) reduces to

$$S = \sum_{\mathrm{R}} S_{\mathrm{R}}, \quad S_{\mathrm{R}} = \sum_{j} (-k_{\mathrm{B}} p_j \ln p_j) \omega_{j\mathrm{R}} \ . \tag{39}$$

It should be noted that the regional entropies S_{R} are exactly added to give the total entropy S, but the maximum of the total entropy S is not necessarily that of the regional entropies.

The alternative density functional representation of E can now be obtained in terms of the regional ones

$$E[\rho] = F[\rho] + \int dr\rho(r)v(r) = \sum_{\mathrm{R}} E_{\mathrm{R}}[\rho] \ , \tag{40}$$

with

$$E_{\mathrm{R}}[\rho] = F_{\mathrm{R}}[\rho] + \int dr\rho_{\mathrm{R}}(r)v(r) \ , \tag{41}$$

and in terms of $E_j[\rho]$ as

$$E_j[\rho] = F_j[\rho] + \int dr\rho_j(r)v(r) = \sum_{\mathrm{R}} E_{j\mathrm{R}}[\rho] \ , \tag{42}$$

with

$$E_{j\mathrm{R}}[\rho] = F_{j\mathrm{R}}[\rho] + \int dr\rho_{j\mathrm{R}}(r)v(r). \tag{43}$$

2.3 Infinitesimal changes in regional quantities

The infinitesimal change of E_{R} is given by

$$dE_{\mathrm{R}} = d\sum_{j} p_j E_{j\mathrm{R}} = \sum_{j} dp_j E_{j\mathrm{R}} + \sum_{j} p_j\, dE_{j\mathrm{R}} \ . \tag{44}$$

For (1) the quantities related to dp_j we have also dN_{R} and dS_{R} as follows:

$$\begin{aligned} dN_{\mathrm{R}} &= d\sum_{j} p_j N_j \omega_{j\mathrm{R}} \\ &= \sum_{j} dp_j N_j \omega_{j\mathrm{R}} + \sum_{j} p_j N_j\, d\omega_{j\mathrm{R}} \ , \end{aligned} \tag{45}$$

$$\begin{aligned} T_{\mathrm{R}}\, dS_{\mathrm{R}} &= T_{\mathrm{R}} d \sum_j (-k_{\mathrm{B}} p_j \ln p_j)\omega_{j\mathrm{R}} \\ &= -k_{\mathrm{B}} T_{\mathrm{R}} \sum_j (dp_j \ln p_j)\omega_{j\mathrm{R}} \\ &\quad -k_{\mathrm{B}} T_{\mathrm{R}} \sum_j [dp_j \omega_{j\mathrm{R}} + (p_j \ln p_j) d\omega_{j\mathrm{R}}] \ , \end{aligned} \tag{46}$$

while for (2) the quantities related to $dE_{j\mathrm{R}}$ we have

$$dE_{j\mathrm{R}} = dF_{j\mathrm{R}} + \int dr\, d\rho_{j\mathrm{R}}(r) v(r) + \int dr \rho_{j\mathrm{R}}(r) dv(r) \ . \tag{47}$$

Here we can write

$$dF_{j\mathrm{R}} + \int dr\, d\rho_{j\mathrm{R}}(r) v(r) = \frac{\partial E_{j\mathrm{R}}}{\partial N_{\mathrm{R}}} dN_{\mathrm{R}} + \sum_{R'(\neq R)} \frac{\partial E_{j\mathrm{R}}}{\partial N_{\mathrm{R'}}} dN_{\mathrm{R'}} \ , \tag{48}$$

where the partial derivatives with respect to the regional electron numbers are to be performed using the manipulation

$$\frac{\partial}{\partial N_{\mathrm{R}}} = \int dr \frac{\partial \rho(r)}{\partial N_{\mathrm{R}}} \frac{\delta}{\delta \rho(r)}, \quad \frac{\partial}{\partial N_{\mathrm{R'}}} = \int dr \frac{\partial \rho(r)}{\partial N_{\mathrm{R'}}} \frac{\delta}{\delta \rho(r)} \ , \tag{49}$$

where δ denotes the functional derivative and

$$\begin{aligned} \frac{\partial \rho(r)}{\partial N_{\mathrm{R}}} &= \left(\frac{\partial \rho(r)}{\partial N_{\mathrm{R}}}\right)_{v, N_{\mathrm{R'}(\neq R)}} , \\ \frac{\partial \rho(r)}{\partial N_{\mathrm{R'}}} &= \left(\frac{\partial \rho(r)}{\partial N_{\mathrm{R'}}}\right)_{v, N_{\mathrm{R'}}, N_{\mathrm{R''}(\neq \mathrm{R},\mathrm{R'})}} \end{aligned} \tag{50}$$

denote the Fukui functions with respect to the regional electron number changes. These are combined to reduce Eq. (44) to

$$\begin{aligned} dE_{\mathrm{R}} &= T_{\mathrm{R}}\, dS_{\mathrm{R}} + \mu_{\mathrm{R}}\, dN_{\mathrm{R}} + \sum_{\mathrm{R'}(\neq R)} \alpha_{\mathrm{RR'}}\, dN_{\mathrm{R'}} \\ &\quad + \int dr \rho_{\mathrm{R}}(r)\, dv(r) \ , \end{aligned} \tag{51}$$

with

$$\begin{aligned} \mu_{\mathrm{R}} &= \mu_{\mathrm{GR}} + k_{\mathrm{B}} T_{\mathrm{R}} \sum_j \left((1 - \Xi_{\mathrm{R}}) \omega_{j\mathrm{R}} \frac{\partial p_j}{\partial N_{\mathrm{R}}} \right. \\ &\quad \left. + (p_j \ln p_j + \gamma_R p_j N_j) \frac{\partial \omega_{jR}}{\partial N_{\mathrm{R}}} \right) + \sum_j p_j \frac{\partial E_{j\mathrm{R}}}{\partial N_{\mathrm{R}}} \ , \end{aligned} \tag{52}$$

$$\begin{aligned} \alpha_{\mathrm{RR'}} &= k_{\mathrm{B}} T_{\mathrm{R}} \sum_j \left((1 - \Xi_{\mathrm{R}}) \omega_{j\mathrm{R}} \frac{\partial p_j}{\partial N_{\mathrm{R'}}} \right. \\ &\quad \left. + (p_j \ln p_j + \gamma_R p_j N_j) \frac{\partial \omega_{jR}}{\partial N_{\mathrm{R'}}} \right) + \sum_j p_j \frac{\partial E_{j\mathrm{R}}}{\partial N_{\mathrm{R'}}} \ . \end{aligned} \tag{53}$$

The regional chemical potential μ_{R} is slightly different from the Gibbs chemical potential μ_{GR}, and the new quantity $\alpha_{\mathrm{RR'}}$ measures the quantum mechanical interference effect. The last term Eq. (51) represents the external work against the nuclear subsystem of A.

3 Chemical equilibrium

If the global chemical equilibrium is attained, we have

$$T_{\mathrm{R}} = T_{\mathrm{R'}} = T_{\mathrm{R''}} = \cdots = T \tag{54}$$

and

$$dE = T\, dS + \mu_{\mathrm{G}}\, dN + \int dr \rho(r) dv(r) \ . \tag{55}$$

Using Eqs. (36), (51), and (54), we have

$$\begin{aligned} dE &= \sum_{\mathrm{R}} dE_{\mathrm{R}} = T \sum_{\mathrm{R}} dS_{\mathrm{R}} + \sum_{\mathrm{R}} \left(\mu_{\mathrm{R}} + \sum_{\mathrm{R'}(\neq \mathrm{R})} \alpha_{\mathrm{R'R}} \right) dN_{\mathrm{R}} \\ &\quad + \int dr \sum_{\mathrm{R}} \rho_{\mathrm{R}}(r)\, dv(r) \ . \end{aligned} \tag{56}$$

Then, comparing Eq. (55) with Eq. (56), and using Eq. (38), we obtain

$$\mu_{\mathrm{G}} = \mu_{\mathrm{R}} + \sum_{\mathrm{R'}(\neq \mathrm{R})} \alpha_{\mathrm{R'R}} \ . \tag{57}$$

This is referred to as the quantum mechanical law of mass action. If we neglect the quantum mechanical interference term $\alpha_{\mathrm{R'R}}$, we get

$$\mu_{\mathrm{R}} = \mu_{\mathrm{R'}} = \mu_{\mathrm{R''}} = \cdots = \mu_{\mathrm{G}} \ , \tag{58}$$

which is nothing but the Gibbs law of mass action. It is observed that Eq. (58) is interpreted as the Sanderson principle of electronegativity equalization [13].

4 Two-region problem

For the illustration of the present treatment, we shall apply the theory to a two-region problem; the system is composed of only two complementary regions Q and P in which an electron is transferred from Q to P. The partitioning of $\rho(r)$, E, N, and S are given by

$$\rho(r) = \rho_{\mathrm{P}}(r) + \rho_{\mathrm{Q}}(r) \ , \tag{59}$$

$$E = E_{\mathrm{P}} + E_{\mathrm{Q}} \ , \tag{60}$$

$$N = N_{\mathrm{P}} + N_{\mathrm{Q}} \ , \tag{61}$$

$$S = S_{\mathrm{P}} + S_{\mathrm{Q}} \ . \tag{62}$$

For the adiabatic process, where the electronic subsystem of A is closed and the external work left in the last term in Eq. (56) is the only work done, we have

$$dN = dN_{\mathrm{P}} + dN_{\mathrm{Q}} = 0 \tag{63}$$

and

$$\begin{aligned} dE = dE_{\mathrm{P}} + dE_{\mathrm{Q}} &= \int dr \rho_{\mathrm{P}}(r) dv(r) + \int dr \rho_{\mathrm{Q}}(r) dv(r) \\ &= \int d(r) \rho(r) dv(r) \ . \end{aligned} \tag{64}$$

Let us define the adiabatic electron transfer across the interface as dn_{Q}:

$$dN_{\mathrm{P}} = -dN_{\mathrm{Q}} = dn_{\mathrm{Q}} > 0 \tag{65}$$

and the adiabatic heat transfer across the interface as dx_{Q}:

$$dQ_{\mathrm{P}} = -dQ_{\mathrm{Q}} = dx_{\mathrm{Q}} \ . \tag{66}$$

Using Eqs. (41), (51), (65), and (66), we have

$$\begin{aligned} dQ_{\mathrm{P}} &= dF_{\mathrm{P}} + \int dr\, d\rho_{\mathrm{P}}(r)v(r) = dx_{\mathrm{Q}} \\ &= T_{\mathrm{P}}\, dS_{\mathrm{P}} + \left(\mu_{\mathrm{P}} - \alpha_{\mathrm{PQ}}\right)dn_{\mathrm{Q}} \ , \end{aligned} \tag{67}$$

$$\begin{aligned} dQ_{\mathrm{Q}} &= dF_{\mathrm{Q}} + \int drd\rho_{\mathrm{Q}}(r)v(r) = -dx_{\mathrm{Q}} \\ &= T_{\mathrm{Q}}\, dS_{\mathrm{Q}} - \left(\mu_{\mathrm{Q}} - \alpha_{\mathrm{QP}}\right)dn_{\mathrm{Q}} \ . \end{aligned} \tag{68}$$

Then the regional entropy production is calculated to be

$$dS_{\mathrm{P}} = \frac{dx_{\mathrm{Q}}}{T_{\mathrm{P}}} - \frac{\mu_{\mathrm{P}} - \alpha_{\mathrm{PQ}}}{T_{\mathrm{P}}} dn_{\mathrm{Q}} \ , \tag{69}$$

$$dS_{\mathrm{Q}} = -\frac{dx_{\mathrm{Q}}}{T_{\mathrm{Q}}} + \frac{\mu_{\mathrm{Q}} - \alpha_{\mathrm{QP}}}{T_{\mathrm{Q}}} dn_{\mathrm{Q}} \ , \tag{70}$$

and the entropy production as a whole is found to be

$$\begin{aligned} dS &= dS_{\mathrm{P}} + dS_{\mathrm{Q}} \\ &= \left(\frac{1}{T_{\mathrm{P}}} - \frac{1}{T_{\mathrm{Q}}}\right)dx_{\mathrm{Q}} - \left(\frac{\mu_{\mathrm{P}}}{T_{\mathrm{P}}} - \frac{\mu_{\mathrm{Q}}}{T_{\mathrm{Q}}} - \left(\frac{\alpha_{\mathrm{PQ}}}{T_{\mathrm{P}}} - \frac{\alpha_{\mathrm{QP}}}{T_{\mathrm{Q}}}\right)\right)dn_{\mathrm{Q}} \ . \end{aligned} \tag{71}$$

In the limit of a small temperature difference, we shall introduce a symbol Δ_{R} which denotes the regional change at the region R and we obtain

$$\begin{aligned} dS = \Delta_{\mathrm{Q}}\left(\frac{1}{T}\right)dq_{\mathrm{Q}} - \frac{1}{T_{\mathrm{Q}}}&\left(\Delta_{\mathrm{Q}}(\mu_{\mathrm{Q}})_{T_{\mathrm{Q}}}\right. \\ &\left. - \left(\Delta_{\mathrm{P}}(\alpha_{\mathrm{PQ}})_{T_{\mathrm{P}}} - \Delta_{\mathrm{P}}(\alpha_{\mathrm{QP}})_{T_{\mathrm{P}}}\right)\right)dn_{\mathrm{Q}} \ , \end{aligned} \tag{72}$$

where the net heat transfer is denoted as dq_{Q}:

$$\begin{aligned} dq_{\mathrm{Q}} &= dx_{\mathrm{Q}} \\ &\quad + \left(-\mu_{\mathrm{Q}} + T_{\mathrm{Q}}\frac{\partial\mu_{\mathrm{Q}}}{\partial T_{\mathrm{Q}}} - T_{\mathrm{Q}}\left(\frac{\partial\alpha_{\mathrm{PQ}}}{\partial T_{\mathrm{P}}} - \frac{\partial\alpha_{\mathrm{QP}}}{\partial T_{\mathrm{P}}}\right)\right)dn_{\mathrm{Q}} \ . \end{aligned} \tag{73}$$

The regional dissipation function $T_{\mathrm{R}}\Theta_{\mathrm{R}}$ for entropy production is then calculated, using a symbol $\mathrm{grad}_{\mathrm{R}}$ which denotes the regional gradient at the region R, to be

$$\Theta_{\mathrm{Q}} = \mathrm{grad}_{\mathrm{Q}}\left(\frac{dS_{\mathrm{Q}}}{dt}\right) \ , \tag{74}$$

$$T_{\mathrm{Q}}\Theta_{\mathrm{Q}} = \sum_{k_{\mathrm{Q}}} X_{k_{\mathrm{Q}}} J_{k_{\mathrm{Q}}} \ , \tag{75}$$

where the generalized force $X_{k_{\mathrm{Q}}}$ and the conjugate flux $J_{k_{\mathrm{Q}}}$ are defined as

$$X_{q_{\mathrm{Q}}} = -\mathrm{grad}_{\mathrm{Q}} \ln(T_{\mathrm{Q}}), \quad J_{q_{\mathrm{Q}}} = \frac{dq_{\mathrm{Q}}}{dt} \ , \tag{76}$$

$$\begin{aligned} X_{n_{\mathrm{Q}}} &= -\mathrm{grad}_{\mathrm{Q}}\left(\mu_{\mathrm{Q}}\right)_{T_{\mathrm{Q}}} + \mathrm{grad}_{\mathrm{P}}\left(\alpha_{\mathrm{PQ}}\right)_{T_{\mathrm{P}}} - \mathrm{grad}_{\mathrm{P}}\left(\alpha_{\mathrm{QP}}\right)_{T_{\mathrm{P}}}, \\ J_{n_{\mathrm{Q}}} &= \frac{dn_{\mathrm{Q}}}{dt} \ . \end{aligned} \tag{77}$$

The regional electron transferability or the regional conductance is calculated by modifying the Kubo formula [14] as follows

$$\Sigma_{\mathrm{Q}} = D_{\mathrm{Q}}S_{\mathrm{Q}}, \quad S_{\mathrm{Q}} = \frac{1}{2\eta_{\mathrm{Q}}}, \quad 2\eta_{\mathrm{Q}} = \frac{\partial\mu_{\mathrm{Q}}}{\partial N_{\mathrm{Q}}} \ , \tag{78}$$

where $D_{\mathrm{Q}}S_{\mathrm{Q}}$, and η_{Q} denote, respectively, the diffusion constant, the absolute softness, and the absolute hardness [15] defined for the region R. The transition state of the chemical reaction can now be postulated to be the one that corresponds to the nuclear framework in which a particular region possesses the maximum regional electron transferability. This postulate has been numerically demonstrated in some ion-molecule chemical reaction systems to encompass the conventional definition of the transition state as the saddle point of the potential energy surface along the IRC [16]. We need to study further the relationship of the concept of the electron transferability and the concept of the transition state that determines the critical point of the electronic process of chemical reactivity.

A case of irreversible electron transfer could be observed under the condition of constant temperature:

$$T_{\mathrm{P}} = T_{\mathrm{Q}} = T \ . \tag{79}$$

For the irreversible process to occur, the entropy production should be positive, $dS > 0$. The formula is found from Eq. (71) to be

$$dS = -\frac{1}{T}\left(\mu_{\mathrm{P}} - \mu_{\mathrm{Q}} - \left(\alpha_{\mathrm{PQ}} - \alpha_{\mathrm{QP}}\right)\right)dn_{\mathrm{Q}} > 0 \ , \tag{80}$$

and then we have

$$\mu_{\mathrm{P}} + \alpha_{\mathrm{QP}} < \mu_{\mathrm{Q}} + \alpha_{\mathrm{PQ}} \ . \tag{81}$$

This is the quantum mechanical criterion of irreversible electron transfer from Q to P at constant temperature, Eq. (79).

A particular adiabatic process of great concern in the electronic theory of chemical reactivity is the quasi-static process defined as

$$dS = dS_{\mathrm{P}} + dS_{\mathrm{Q}} = 0,\ T_{\mathrm{P}} = T_{\mathrm{Q}} = T \ , \tag{82}$$

and hence from Eq. (80) we conclude

$$\mu_{\mathrm{P}} + \alpha_{\mathrm{QP}} = \mu_{\mathrm{Q}} + \alpha_{\mathrm{PQ}} \ . \tag{83}$$

This again confirms Eq. (57) and hence is written explicitly as

$$\mu_{\mathrm{G}} = \mu_{\mathrm{P}} + \alpha_{\mathrm{QP}} = \mu_{\mathrm{Q}} + \alpha_{\mathrm{PQ}} \ . \tag{84}$$

In this case, the entropy production disappears and therefore, we concentrate solely on the change in the regional electron numbers. Let us then introduce the coordinate of electron transfer Γ that is a function $g(x)$ of $x = N_{\mathrm{P}} - N_{\mathrm{Q}}$ [3]:

$$\Gamma = g(N_{\mathrm{P}} - N_{\mathrm{Q}}) \ . \tag{85}$$

The change in E with respect to Γ has been referred to as the excitation potential ε [3]:

$$\varepsilon = \left(\frac{\partial E}{\partial \Gamma}\right)_{S,N,v} \tag{86}$$

The partitioning of ε is given by

$$\varepsilon = \varepsilon_{\mathrm{P}} + \varepsilon_{\mathrm{Q}} \ , \tag{87}$$

where the regional excitation potentials are defined as

$$\varepsilon_{\mathrm{P}} = \left(\frac{\partial E_{\mathrm{P}}}{\partial \Gamma}\right)_{S,N,v}, \quad \varepsilon_{\mathrm{Q}} = \left(\frac{\partial E_{\mathrm{Q}}}{\partial \Gamma}\right)_{S,N,v} \ , \tag{88}$$

which are now calculated to be

$$\varepsilon_{\mathrm{P}} = \frac{dQ_{\mathrm{P}} - T\,dS_{\mathrm{P}}}{d\Gamma} \ , \tag{89}$$

$$\varepsilon_{\mathrm{Q}} = \frac{dQ_{\mathrm{Q}} - T\,dS_{\mathrm{Q}}}{d\Gamma} \ . \tag{90}$$

Using Eqs. (67), (68), (89), and (90), we obtain

$$\begin{aligned} dQ_{\mathrm{P}} &= dF_{\mathrm{P}} + \int dr\, d\rho_{\mathrm{P}}(r) v(r) \\ &= T\,dS_{\mathrm{P}} + \varepsilon_{\mathrm{P}}\,d\Gamma = T\,dS_{\mathrm{P}} + \left(\mu_{\mathrm{P}} - \alpha_{\mathrm{PQ}}\right) dn_{\mathrm{Q}} \ , \end{aligned} \tag{91}$$

$$\begin{aligned} dQ_{\mathrm{Q}} &= dF_{\mathrm{Q}} + \int dr\, d\rho_{\mathrm{Q}}(r) v(r) \\ &= T\,dS_{\mathrm{Q}} + \varepsilon_{\mathrm{Q}}\,d\Gamma = T\,dS_{\mathrm{Q}} - \left(\mu_{\mathrm{Q}} - \alpha_{\mathrm{QP}}\right) dn_{\mathrm{Q}} \ , \end{aligned} \tag{92}$$

The excitation potential as a whole then vanishes:

$$\varepsilon = \varepsilon_{\mathrm{P}} + \varepsilon_{\mathrm{Q}} = \left(\frac{\partial E}{\partial \Gamma}\right)_{S,N,v} = 0 \ , \tag{93}$$

where Eqs. (91) and (92) have been added and Eqs. (82) and (83) have been used. Alternatively, using Eqs. (66), (82), (89), and (90), we have Eq. (93).

On the other hand, introducing the transfer potentials [4]

$$\tau_{\mathrm{P}} = \left(\frac{\partial E_{\mathrm{P}}}{\partial N}\right)_{S,\Gamma,v}, \quad \tau_{\mathrm{Q}} = \left(\frac{\partial E_{\mathrm{Q}}}{\partial N}\right)_{S,\Gamma,v} \ , \tag{94}$$

we have the sum rule as follows:

$$\mu_{\mathrm{G}} = \tau_{\mathrm{P}} + \tau_{\mathrm{Q}} = \left(\frac{\partial E}{\partial N}\right)_{S,\Gamma,v} \ , \tag{95}$$

where we have used Eqs. (4) and (93).

The transfer potentials are combined to prove another rule, the difference rule. Here we consider the process of nonzero dN under the quasi-static condition of Eq. (82). Then, using Eqs. (41), (51), (88), and (94), we have

$$\begin{aligned} dQ_{\mathrm{P}} &= dF_{\mathrm{P}} + \int dr\, d\rho_{\mathrm{P}}(r) v(r) \\ &= T\,dS_{\mathrm{P}} + \mu_{\mathrm{P}}\,dN_{\mathrm{P}} + \alpha_{\mathrm{PQ}}\,dN_{\mathrm{Q}} \\ &= T\,dS_{\mathrm{P}} + \tau_{\mathrm{P}}\,dN + \varepsilon_{\mathrm{P}}\,d\Gamma \ , \end{aligned} \tag{96}$$

$$\begin{aligned} dQ_{\mathrm{Q}} &= dF_{\mathrm{Q}} + \int dr\, d\rho_{\mathrm{Q}}(r) v(r) \\ &= T\,dS_{\mathrm{Q}} + \mu_{\mathrm{Q}}\,dN_{\mathrm{Q}} + \alpha_{\mathrm{QP}}\,dN_{\mathrm{P}} \\ &= T\,dS_{\mathrm{Q}} + \tau_{\mathrm{Q}}\,dN + \varepsilon_{\mathrm{Q}}\,d\Gamma \ . \end{aligned} \tag{97}$$

Here we use Eqs. (61) and (85) to obtain the relationship

$$dN = dN_{\mathrm{P}} + dN_{\mathrm{Q}} \ , \tag{98}$$

$$d\Gamma = g'\left(dN_{\mathrm{P}} - dN_{\mathrm{Q}}\right) \ , \tag{99}$$

and substituting Eqs. (98) and (99) into Eqs. (96) and (97), we obtain

$$\mu_{\mathrm{P}} = \tau_{\mathrm{P}} + g'\varepsilon_{\mathrm{P}}, \quad \alpha_{\mathrm{PQ}} = \tau_{\mathrm{P}} - g'\varepsilon_{\mathrm{P}} \ , \tag{100}$$

$$\mu_{\mathrm{Q}} = \tau_{\mathrm{Q}} - g'\varepsilon_{\mathrm{Q}}, \quad \alpha_{\mathrm{QP}} = \tau_{\mathrm{Q}} + g'\varepsilon_{\mathrm{Q}} \ . \tag{101}$$

We therefore prove a couple of difference rules

$$\mu_{\mathrm{P}} - \mu_{\mathrm{Q}} = \tau_{\mathrm{P}} - \tau_{\mathrm{Q}} \ , \tag{102}$$

$$\alpha_{\mathrm{PQ}} - \alpha_{\mathrm{QP}} = \tau_{\mathrm{P}} - \tau_{\mathrm{Q}} \ , \tag{103}$$

where we have subtracted Eq. (101) from Eq. (100) and have used Eq. (93). The second difference rule, Eq. (103), can also be deduced from Eqs. (83) and (102). Thus Eqs. (95) and (102) constitute the regional chemical potential inequality principle as shown in Fig. 1.

We shall here augment Eqs. (98) and (99) with some useful relationships as follows:

$$dN_{\mathrm{P}} = \frac{1}{2}\left(dN + \frac{d\Gamma}{g'}\right) \ , \tag{104}$$

$$dN_{\mathrm{Q}} = \frac{1}{2}\left(dN - \frac{d\Gamma}{g'}\right) \ , \tag{105}$$

and

$$\frac{\partial}{\partial N} = \frac{1}{2}\frac{\partial}{\partial N_{\mathrm{P}}} + \frac{1}{2}\frac{\partial}{\partial N_{\mathrm{Q}}} \ , \tag{106}$$

$$\frac{\partial}{\partial \Gamma} = \frac{1}{2g'}\frac{\partial}{\partial N_{\mathrm{P}}} - \frac{1}{2g'}\frac{\partial}{\partial N_{\mathrm{Q}}} \ , \tag{107}$$

5 Example

As an example, we take the limit of $T = 0$. Then the density matrix reduces to that of the pure state corresponding to a particular ground state of fixed electron number, say $E = E_0$ and $N = N_0$ for the zeroth state. We have then the regional energy

$$E_{\mathrm{R}} = E\frac{N_{\mathrm{R}}}{N} = \frac{E}{N}N_{\mathrm{R}} \ . \tag{108}$$

That the regional energy is proportional to the regional electron number is rigorously true in this limit. For a closed system in the two-region problem under the quasi-static condition of Eq. (82), the differentials of Eq. (108) give

$$\varepsilon_{\mathrm{P}} = \frac{1}{2g'}\frac{E}{N} + \frac{N_{\mathrm{P}}}{N}\int dr \rho_{\mathrm{Q}}(r)\frac{dv(r)}{d\Gamma} - \frac{N_{\mathrm{Q}}}{N}\int dr \rho_{\mathrm{P}}(r)\frac{dv(r)}{d\Gamma} \ ,$$

$$\varepsilon_{\mathrm{Q}} = -\frac{1}{2g'}\frac{E}{N} + \frac{N_{\mathrm{Q}}}{N}\int dr\rho_{\mathrm{P}}(r)\frac{dv(r)}{d\Gamma} - \frac{N_{\mathrm{P}}}{N}\int dr\rho_{\mathrm{Q}}(r)\frac{dv(r)}{d\Gamma} \ , \tag{109}$$

where we have used Eqs. (104) and (105). Therefore, substituting Eq. (109) into Eqs. (100) and (101), we get

$$\begin{aligned}\mu_{\mathrm{P}} &= \tau_{\mathrm{P}} + \frac{1}{2}\frac{E}{N} \\ &\quad + g'\left(\frac{N_{\mathrm{P}}}{N}\int dr\rho_{\mathrm{Q}}(r)\frac{dv(r)}{d\Gamma} - \frac{N_{\mathrm{Q}}}{N}\int dr\rho_{\mathrm{P}}(r)\frac{dv(r)}{d\Gamma}\right), \\ \alpha_{\mathrm{PQ}} &= \tau_{\mathrm{P}} - \frac{1}{2}\frac{E}{N} \\ &\quad - g'\left(\frac{N_{\mathrm{P}}}{N}\int dr\rho_{\mathrm{Q}}(r)\frac{dv(r)}{d\Gamma} - \frac{N_{\mathrm{Q}}}{N}\int dr\rho_{\mathrm{P}}(r)\frac{dv(r)}{d\Gamma}\right) \ ,\end{aligned} \tag{110}$$

$$\begin{aligned}\mu_{\mathrm{Q}} &= \tau_{\mathrm{Q}} + \frac{1}{2}\frac{E}{N} \\ &\quad - g'\left(\frac{N_{\mathrm{Q}}}{N}\int dr\rho_{\mathrm{P}}(r)\frac{dv(r)}{d\Gamma} - \frac{N_{\mathrm{P}}}{N}\int dr\rho_{\mathrm{Q}}(r)\frac{dv(r)}{d\Gamma}\right), \\ \alpha_{\mathrm{QP}} &= \tau_{\mathrm{Q}} - \frac{1}{2}\frac{E}{N} \\ &\quad + g'\left(\frac{N_{\mathrm{Q}}}{N}\int dr\rho_{\mathrm{P}}(r)\frac{dv(r)}{d\Gamma} - \frac{N_{\mathrm{P}}}{N}\int dr\rho_{\mathrm{Q}}(r)\frac{dv(r)}{d\Gamma}\right) \ ,\end{aligned} \tag{111}$$

Moreover, for free electrons for which

$$v(r) = 0 \ , \tag{112}$$

and using the independent-particle model, we have the equality

$$\mu_{\mathrm{G}} = \frac{E}{N} = \mathrm{const}, \quad E_{\mathrm{P}} = \mu_{\mathrm{G}}N_{\mathrm{P}}, \quad E_{\mathrm{Q}} = \mu_{\mathrm{G}}N_{\mathrm{Q}} \ . \tag{113}$$

Then we get

$$dE_{\mathrm{P}} = \mu_{\mathrm{G}}\, dN_{\mathrm{P}}, \quad dE_{\mathrm{Q}} = \mu_{\mathrm{G}}\, dN_{\mathrm{Q}} \ , \tag{114}$$

and hence

$$\tau_{\mathrm{P}} = \frac{1}{2}\mu_{\mathrm{G}}, \quad \tau_{\mathrm{Q}} = \frac{1}{2}\mu_{G} \ , \tag{115}$$

$$\varepsilon_{\mathrm{P}} = \frac{1}{2g'}\mu_{\mathrm{G}}, \quad \varepsilon_{\mathrm{Q}} = -\frac{1}{2g'}\mu_{\mathrm{G}} \ , \tag{116}$$

where we have used Eqs. (106) and (107). Equation (116) is also given by substituting Eq. (112) into Eq. (109). Moreover, using Eqs. (100) and (101), we obtain

$$\mu_{\mathrm{P}} = \mu_{\mathrm{Q}} = \mu_{\mathrm{G}}, \quad \alpha_{\mathrm{PQ}} = \alpha_{\mathrm{QP}} = 0 \ . \tag{117}$$

Likewise, substituting Eq. (112) into Eqs. (110) and (111), we get Eq. (117). The constancy of the regional chemical potentials and the vanishing of the coherency terms, Eq. (117), reflect the homogeneity of the electron density $\rho(r)$ and the absence of the quantum mechanical interference effects.

6 Conclusion

Regional density functional theory has been extended to treat irreversible thermodynamic electronic processes for application to adiabatic electron transfer processes of chemical reactions. Onsager's local equilibrium hypothesis is slightly modified to take into account the quantum mechanical nature of the electron. The quantum mechanical interference effect has been demonstrated to be included in the entropy production rate formula associated with electron transfer through an interface. The new concept of regional electron transferability is proposed and the determination of the transition state of a chemical reaction has been postulated that corresponds to the maximum of the regional electron transferability. A quantum mechanical law of mass action has been established and applied to prove the chemical potential inequality principle. The new quantum mechanical principle predicts the inequality between either

1. The Fermi level and the regional chemical potential, or
2. The regional chemical potentials themselves.

As an example of the present theory, the zero-temperature limit and the free-electron model have been demonstrated.

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