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A Second Variation of the Energy Functional: Frontier Functions for Rydberg Atoms

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We introduce a density-functional approach to calculate electron transfer (ET) between atoms during a process of reaction or collision. Charge transfer of this kind is due entirely to differences of chemical potentials that are quantities relevant in the density-functional formalism, statistical mechanics, and thermodynamics. ET here is independent of electromagnetic interactions if we disregard their influences on the chemical potential. This subject still under intensive investigation in physics is attributed to the transition state described in the Franck-Condon principle. After introducing the main theory, we calculate frontier functions for hydrogen-like and helium-like atoms. Results of single-atom systems confirm concepts of the density of states or accumulations of electrons in semiconductor physics, many-body theories etc., but they imply more physics, particularly in statistical mechanics, about such accumulation from results of two-atom cases.

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I. INTRODUCTION

The state of the electron has been a research topic for nearly a century since the development of atomic physics and quantum mechanics. It has been proposed to be an orbital, a wave funciton, an occupation number state, electron density etc. When we encounter problems involving two nuclei such as in molecular physics we use twocenter situations (integrals) and evolve the idea of covalent bonds. Bonding concepts are actively used in chemistry. In physics, single electrons are still treated individually (e.g. in the Hamiltonian formalism in the beginning). The share of an electron (as its density) is attributed to charge transfer instead of assigning fractions of a single electron to other centers. The physical explanation is attributed to the Franck-Condon principle, viz., the duration of reaction is less than that of a quantum jump.

A researcher on electron transfer (ET) has his own reputation in chemistry and recently won the Nobel prize [1]. In the original concepts charges were kept as integer multiples of electronic charge. During a chemical reaction, charges fluctuate, unable to maintain integer transfer of electronic charge [1]. The initial reactants and final products still have integer numbers of electrons although they are not quantum jumps. Continuous charge transfer seems necessary and leads us to use density-functional theory (DFT). The most important quantity in DFT is the chemical potential, as important as in statistical mechanics and thermodynamics. Applications of DFT in ET are topics investigated in detail by physicists and chemists in recent years, and are the main subject that we here review. The accepted conception of the chemical potential is that it is constant *over* the substance in a *discrete sense, e.g.* for one particle added or extracted. Therefore we have various points of view about the fact that the chemical potential is the first variation of the total energy functional as given in DFT. In current research on quantum cricuits, or alternatively artificial atoms [2], we encounter exactly the same physical situation. We may use the same way to treat the statics and dynamics of these systems.

Further developments lead us to inquire about the second derivative of the total energy functional that has become known as “hardness”. We remain at a stage at which we inquire what is the second variation with respect to densities in mathematics, e.g. whether kernel functions, physical observables, etc. We even inquire about manipulations of the second derivative of a functional. The second interest is on simple quantized systems such as atoms and molecules. What happens to this hardness? Instead of providing a definitive answer, we review the current situation. Because most theories imply chemistry or chemical physics and were developed only recently, it is worth while to introduce them here.

For hard and soft acids and bases, the theory of Pearson [3] begins with two functions, viz., μ (chemical potential) and η (hardness) to describe molecular behaviour during chemical reactions. If there is a reaction $A + B \rightleftharpoons A : B$, say, for the Lewis acid A and base B, how do we know whether electrons flow from A to B or from B to A. In Ref. [3], Pearson concluded that this tendency is determined by values of μ. The second question is the number of electrons that flow. The value of η becomes included to decide the number of electrons that flow. The hardness η is a second derivative of the total energy with respect to N. These two quantities are relevant also to physics, for instance, in semiconductor screening [4], determination of the Fermi energy [5] etc. It is natural to extend the concept to electronic occupation of a nucleus, such as in stationary states [6], electron-nucleus scattering, charge transfer in quantum dots with Coulomb blockade [7], high-T, superconductors under pressure etc.

In physics, in a further step of development we invoke concepts of anti-particles. Thereby, we propose the hole concept to manipulate states of negative energy electron. Hence arises the hole state incorporated into electron charge states. The recombination process is an active subject of research for decades, e.g. recombination of positron with electron in positron annihilation, electron and hole recombination in photoluminescence in solid-state lasers, ion and electron recombination in semiconductors, [8] etc. They are closely related to charge transfer of integer numbers of electrons.

Next in this report, we review variational quantities in DFT. Then we calculate the frontier function for hydrogen-like and helium-like atoms in six cases. We find this function to be essentially the density per electron in single-atom cases. This conclusion leads us to understand the accumulation of electrons as a local density of states in semiconductor physics from the point of view of chemical physics. If we invoke the so-called HSAB-principle [9] (i.e. “hard likes hard and soft likes soft”), we can modify current condepts of accumulations of this kind, which becomes complicated for two atoms with ET. Hence the application of these results provides us with new insight into current research.

II. GLOBAL THEORY WITH PARAMETERS: μ AND η

In a system of $\mathcal{N}$ particles, it is known of chemical potentials that [5]

$$\mu_{\mathcal{N}=N} \neq \mu_{\mathcal{N}=N-1} \neq \mu_{\mathcal{N}=N+1}.$$

The determination of μ_N becomes uncertain and depends on various authors. In a more profound way, we may determine μ as follows [3]. Because E is a discrete function of N, we determine μ as

$$\frac{E_N - E_{N+1}}{N - (N+1)} = -(E_N - E_{N+1}) = -A; \quad A = \text{electron affinity} \geq 0 \tag{2.1}$$

$$\frac{E_{N-1} - E_N}{(N - 1) - N} = -(E_{N-1} - E_N) = -I; \quad I = \text{ionization potential} \geq 0 \tag{2.2}$$

$$\mu \equiv \frac{\partial E}{\partial N} \approx -\frac{I + A}{2} \equiv -\chi; \quad \mathbf{X} ❑ \text{ electronegativity} \tag{2.3}$$

in which we consider discrete variations of electron numbers. For a chemical reaction in equilibrium,

$$A_{,,} + B_0 \rightleftharpoons AB$$

chemical potentials $\mu_{A_0} = \mu_{B_0} = \mu_{AB}$. If it is not in equilibrium, $|\mu_{A_0}| > |\mu_{B_0}|$ for instance, electrons flow from B to A. This result can be shown by comparing reactions

$$\begin{cases} AB + \Delta E_1 \rightarrow A+ \ t \ B^- \\ AB + \Delta E_2 \rightarrow A- + B+ \end{cases}$$

and defining the difference AE = $\Delta E_1 - \Delta E_2$. If AE > 0, then $AB \rightarrow A- \ t \ B^+$ is favored. According to definitions $\Delta E_1 = I_A - A_B$, and $\Delta E_2 = I_B - A_A$, *we* obtain

$$\begin{aligned} \Delta E &= (I_A - A_B) - (I_B - A_A) \\ &= 2(\chi_A - \chi_B) . \end{aligned} \qquad (2.4)$$

Therefore when $\chi_A > \chi_B$ or equivalently $|\mu_A| > |\mu_B|$, the product must be $A- + B^+$. To investigate further variations of the energy functional, we define [3]

$$\eta \equiv \frac{1}{2}\frac{\partial \mu}{\partial N} = \frac{1}{2}\frac{\partial^2 E}{\partial N^2} \text{hardness} . \qquad (2.5)$$

From (2.1) and (2.2) for integer variations of electron numbers

$$\eta = \frac{1}{2}(I - A). \qquad (2.5a)$$

For the reaction of Lewis acid A and base B [3]

$$A + : B \rightleftharpoons A : B$$

we expand the energy in powers of ET number δ

$$\begin{aligned} E_A &= E_{A_0} + \frac{\partial E_{A_0}}{\partial N}(N_A - N_{A_0}) \ t \ \frac{1}{2}\frac{\partial^2 E_{A_0}}{\partial N^2}(N_A - N_{A_0})^2 \\ &= E_{A_0} + \mu_{A_0}(N_A - N_{A_0}) + \eta_{A_0}(N_A - N_{A_0})^2 , \\ E_B &= E_{B_0} + \mu_{B_0}(N_B - N_{B_0}) + \eta_{B_0}(N_B - N_{B_0})^2 , \\ N_A &= N_{A_0} + \delta , \quad N_B = N_{B_0} - \delta . \end{aligned} \qquad (2.6)$$

Here we consider charge transfer such that 6 may be fractional or even continuous. We have a degree of freedom to assign which part of charge belongs to *A*. Similarly, we expand μ in powers of δ from (2.5) (for constant potential $v(\vec{r})$ for the frontier function discussed below)

$$\begin{aligned} \mu_A &= \mu_{A_0} + 2\eta_{A_0}\delta , \\ \mu_B &= \mu_{B_0} - 2\eta_{B_0}\delta . \end{aligned} \qquad (2.7)$$

At equilibrium or in the molecule *AB*, $\mu_A = \mu_B$ at the given molecular configuration

$$\delta = \frac{\mu_{B_0} - \mu_{A_0}}{2(\eta_{A_0} + \eta_{B_0})} = \frac{\chi_{A_0} - \chi_{B_0}}{2(\eta_{A_0} + \eta_{B_0})} . \qquad (2.8)$$

Thus 6 is non-integer in general but is determined in terms of quantities in isolated states before the reaction. We are uncertain about the relationship between these quantitites and the condition $v(\vec{r}) =$ constant.

III. LOCAL THEORY WITH PARAMETERS: $\tilde{\eta}(\vec{r})$ AND $\tilde{s}(\vec{r})$

From DFT, for fixed nuclear potential $v(\vec{r})$, the energy is written as a functional of the electron density $\rho(\vec{r})$,

$$E_v[\rho] = \int v(\vec{r})\rho(\vec{r})d\vec{r} + F[\rho] \tag{3.1}$$

$$F[\rho] = T[\rho] + V_{ee}[\rho] \tag{3.2}$$

for the non-interacting electronic kinetic energy functional $T[\rho]$, and the electron-electron interaction energy $V_{ee}[\rho]$. Lagrange ' s multiplier method requires that

$$\delta\{E_v[\rho] - \mu N[\rho]\} = 0\,, \tag{3.3}$$

for the chemical potential μ. From (3.1), it is easy to obtain

$$\begin{aligned} &\mu = v(\vec{r}) + \frac{\delta F}{\delta\rho} = \left[\left(\frac{\delta E[\rho]}{\delta\rho}\right)_v\right]_{\rho=\rho(v)}, \\ &\frac{\delta N}{\delta\rho} = 1\,, \end{aligned} \tag{3.4}$$

where ρ is an independent variable in DFT.

However, in the local thoery, μ is a global parameter, i.e. not a function of coordinates. It depends on N through ρ, and $v(\vec{r})$; i.e. in this review we shall extend the functional behaviours of μ from (2.7) and propose definitely that *the chemical potential is a function of N and a functional of* $v(\vec{r})$. This functional dependency was used throughout the whole theory. In Refs. [10,11], the authors calculated an alternation from one ground state to another ground state. Both these ground states are determined from variations of $E[N,v]$ and $\mu[N,v]$ subject to (3.3). The energy change is

$$\begin{aligned} dE &= \left(\frac{\partial E}{\partial N}\right)_v dN + \int \left(\frac{\delta E}{\delta v}\right)_N \delta v(\vec{r})d\vec{r} \\ &= \mu dN + \int \rho(\vec{r})\delta v(\vec{r})d\vec{r}\,. \end{aligned} \tag{3.5}$$

The ideas in investigations with (3.5) are not familiar in physics. The possibility of an investigation in this way was originally suggested by Parr and Yang [5,6]; they proposed that the variation $\delta v(\vec{r})$ was a perturbation to the external potential: e.g. the nuclear potential is modified externally by a change

$$v(\vec{r}) \Longrightarrow v(\vec{r}) + \textstyle\sum_i \delta v(\vec{r}_i) \tag{3.6}$$

that defines $\delta v(\vec{r})$. From an argument on (3.1) we find

$$\mu = \left(\frac{\partial E}{\partial N}\right)_v ; \qquad \rho(\vec{r}) = \left(\frac{\delta E}{\delta v}\right)_N . \tag{3.7}$$

In a similar manner, we obtain from the functional relation $\mu = \mu[N, v]$,

$$d\mu = 2\eta dN + \int f(\vec{r})\delta v(\vec{r})d\vec{r} \tag{3.8}$$

in which the function $f(\vec{r})$ is defined as

$$f(\vec{r}) \equiv \left(\frac{\delta\mu}{\delta v}\right)_N = \left[\frac{\delta}{\delta v}\left(\frac{\delta E}{\delta N}\right)_v\right]_N = \left(\frac{\partial\rho(\vec{r})}{\partial N}\right)_v . \tag{3.9}$$

The equality in this formula is a Maxwell relation of (3.5). The function $f(\vec{r})$ is called a frontier function or Fukui function.

In the formulation of the density of states at zero temperature, we write the density, $\rho(\vec{r})$ [12]

$$\rho(\vec{r}) = \textstyle\sum_i |\psi_i(\vec{r})|^2 \theta(\mu - \epsilon_i) \tag{3.10}$$

in which $\psi_i\vec{r})$are normalized states. Thus we have

$$\mathrm{N} = \int_0^\mu g(\epsilon)d\epsilon \tag{3.11}$$

and hence

$$\frac{1}{2\eta} = \left(\frac{\partial N}{\partial \mu}\right)_{T,V} = g(\epsilon_F) . \tag{3.12}$$

The latter equation means that, for a metal at absolute zero, the reciprocal of the hardness is twice the density of states at the Fermi level. This result brings us an important idea about the reciprocal of the hardness that we introduce as softness to represent this quantity hereafter.

From surface physics theory, the local density of states $g(\epsilon, \vec{r})$ is defined according to

$$g(\epsilon, \vec{r}) = \Sigma_i |\psi_i(\vec{r})|^2 \delta[\epsilon_i - \epsilon] . \tag{3.13}$$

By analogy with (3.11), we have

$$\mathrm{p(7)} = \int_0^\mu g(\epsilon, \vec{r})d\epsilon \tag{3.14}$$

that leads to

$$\frac{\partial\rho}{\partial\mu} = g(\mu = \epsilon_F, \vec{r}) \tag{3.15}$$

which is the local density of states at the Fermi surface. Consequently, using (3.12), we find from (3.9) [13]

$$\begin{aligned} f(\vec r) &= \left(\frac{\partial\rho(\vec r)}{\partial N}\right)_{T,V} = \left(\frac{\partial\rho(\vec r)}{\partial\mu}\right)_{T,V}\left(\frac{\partial\mu}{\partial N}\right)_{T,V} \\ &= 2\eta g(\epsilon_F,\vec r) = \frac{g(\epsilon_F,\vec r)}{g(\epsilon_F)}\,. \end{aligned} \tag{3.16}$$

The frontier function is the normalized local density of states at the Fermi level. It represents also the possibility of accumulating the quantity of electrons at a point relative to other places in the system. The normalization $\int f(\vec r)d\vec r = 1$ corresponds to $\int g(\epsilon_F,\vec r)d\vec r = g(\epsilon_F)$ from the latter equation. As a remark here, we have considered only the one-electron-Fermi-sea.

We define, for any species, the global softness S as the inverse of global hardness

$$S \equiv \frac{1}{\eta} = 2\left(\frac{\partial N}{\partial\mu}\right)_v, \tag{3.17}$$

thus the local softness $\tilde s(\vec r)$ and local hardness $\tilde\eta(\vec r)$ according to the formulae [13]

$$\begin{aligned} \tilde s(\vec r) &= S f(\vec r) = 2\left(\frac{\partial\rho(\vec r)}{\partial}\right)_{T,v}, \\ \tilde\eta(\vec r) &= \frac{1}{2}\left(\frac{\delta\mu}{\delta\rho}\right)_v, \end{aligned} \tag{3.18}$$

after the density $\rho(\vec r)$ is explicitly introduced as a variable according to

$$N = \int \rho(\vec r)d\vec r.$$

The local softness has directly the integral properties

$$\begin{aligned} \int \tilde s(\vec r)d\vec r &= 2\left(\frac{\partial}{\partial\mu}\int\rho(\vec r)d\vec r\right)_{T,v} = S\,, \\ \int \tilde\eta(\vec r)\tilde s(\vec r)d\vec r &= \int\frac{1}{2}\left(\frac{\delta\mu}{\delta\rho}\right)_v \times 2\left(\frac{\partial\rho}{\partial\mu}\right)_{T,v} d\vec r = 1\,. \end{aligned} \tag{3.19}$$

In the latter equation the chain rule of functional derivatives is used. As a part of local hardness is proportional to the electrostatic potential generated by the charge distribution of a system, from this connection we deduce that the hard-hard interaction during a reaction is related to electrostatic effects [10,14]. In contrast $\tilde s(\vec r)$ contains the same local information as the state at the Fermi level (frontier orbitals). Accordingly, soft-soft *interactions are driven by covalent (orbital) effects in contrast to hard-hard interactions in which one has* ET [9]. Note that (3.19) does not imply that $\tilde s(\vec r)$ and $\tilde\eta(\vec r)$ are reciprocals at each point in space; however, it is expected that regions with small values of local softness are hard regions.

IV. FRONTIER FUNCTIONS IN RYDBERG ATOMS

According to the preceding section, if we can have a frontier function, we can know the relative softness locally from (3.18). According to the HSAB principle described in Sec. I, we know the configuration of reaction, viz., at the places at which reactions are most likely to occur. We proceed to investigate frontier functions in the most transparent atomic systems, hydrogen-like and helium-like atoms. We need to classify systems according to cases: single-atom or two-atom systems, perturbed or unperturbed configurations etc. For the frontier function given in (3.9) there is a restriction to keep the (molecular) potential constant. This restriction evokes the conventional molecular results from the mathematical correctness. Secondly, because ET lack covalent bonding [1], soft-soft interactions are driven by electromagnetic forces, not related to ET. We try to minimize these e.m. forces in order to investigate only ET. Hence, calculations here are more tenable with the definition of frontier function, particularly in the ET part. Covalent bonding appears to be symmetry-broken due to interference of the electric potential in addition to the ET effects. Thus the Thomas-Fermi field theory is a prospective model to take into account both ET and covalent bonding. Further points of view are presented later.

Case I: Simple Hydrogen Atom

First for the Hamiltonian

$$H_H(Z) = -\frac{1}{2}\nabla^2 - \frac{Z}{r}\,, \tag{4.1}$$

the ground-state eigenfunction of H-atom is

$$\Psi_0(Z) = \sqrt{\frac{Z^3}{\pi}}\; e^{-Zr}\,. \tag{4.2}$$

We need a perturbation of this single-atom case, just as in many calculations in DFT. For (3.5), we assign a b-perturbation (a density prober)

$$\begin{aligned} \delta v(\vec{r}) &= G\Theta\,, \\ \Theta &\equiv \begin{cases} 1 & ,\ \text{for } R - \frac{\Delta R}{2} \le r \le R + \frac{\Delta R}{2} \\ 0 & .\ \text{elsewhere} \end{cases} \end{aligned}$$

According to first-order perturbation theory, the energy change is

$$\begin{aligned} E^{(0)} &= \langle \Psi_0(Z) | H_H | \Psi_0(Z) \rangle\,, \\ E^{(1)} &= \langle \Psi_0(Z) | G\Theta | \Psi_0(Z) \rangle\,, \\ dE &= E^{(1)}\,. \end{aligned}$$

We seek the difference of chemical potentials under the above perturbation by (3.8)

$$d\mu = \mu - \mu_0 = 2\eta\Delta N + \int f(\vec{r})G\Theta d\vec{r}, \tag{4.3}$$

for no electron variation in this one-electron atom

$$\mu = \frac{\partial E}{\partial N} = E^{(0)} + E^{(1)}, \quad \mu_0 = E^{(0)};$$

$$d\mu = E^{(1)} = \int f(\vec{r})G\Theta d\vec{r}$$

$$= \int |\Psi_0(\vec{r})|^2 G\Theta d\vec{r} = \mathbf{G} \int_{R-\frac{\Delta R}{2}}^{R+\frac{\Delta R}{2}} f(r)4\pi r^2 dr .$$

Taking a limit process

$$\Delta R \to 0, \quad G \to \infty; \quad \mathrm{GAR} \to \textit{finite},$$

we obtain the frontier function

$$\begin{aligned} f_1(\vec{r}) &= |\Psi_0(Z,\vec{r})|^2 = \rho_0(Z,\vec{r}) \\ & Z^3 \quad {}_{-2Zr} \quad \frac{\rho_0(Z)}{}: \quad N = 1 \end{aligned} \tag{4.4}$$

Therefore the frontier function is not only the derivative of the density with respect to the total number as given in (3.9) but also their direct ratio as given in (4.4).

Case II: Non-intemcting Helium-like Atoms

The Hamiltonian for non-interacting helium-like atoms is

$$H^0_{He} = H_H(1) + H_H(2). \tag{4.5}$$

Here we have as unperturbed case the single-atom system. The state is a simple product of two ground-state wave functions as given in (4.2). To calculate the energy of this atom according to the Ritz variational principle with the trial function

$$\begin{aligned} &\Psi_{He^0}(\vec{r}_1, \vec{r}_2) = \Psi_0(Z_0,\vec{r}_1)\Psi_0(Z_0,\vec{r}_2), \\ &\mathcal{E}^0(Z_0) \equiv \langle H^0_{He}\rangle = Z_0^2 - 2Z_0 Z, \\ &\frac{\delta\mathcal{E}^0}{\delta Z_0} = 0; \quad Z_0 = Z, \end{aligned} \tag{4.6}$$

we obtain one- and twoelectron densities

$$\begin{aligned} \rho_{He^0_1}(\vec{r}) &= \frac{Z^3}{\pi}e^{-2Zr}, \\ \rho_{He^0_2}(\vec{r}) &= 2\frac{Z^3}{\pi}e^{-2Zr}. \end{aligned} \tag{4.7}$$

The simple results given in (4.7) arise because this case is equivalent to the unperturbed case $\delta v = 0$. The frontier function follows from (3.9) for integral ET

$$\begin{aligned} f_2(\vec{r}) &= \frac{\rho_{He_2^0} - \rho_{He_1^0}}{2-1} \\ &= \frac{Z^3}{\pi} e^{-2Zr} = \frac{\rho_{He_2^0}}{2} . \end{aligned} \tag{4.8}$$

Case III: Helium-like Atoms

For complete helium-like atoms, the Hamiltonian is

$$\begin{aligned} H_{He} &= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 \\ V_{ee} &= \frac{1}{r_{12}} . \end{aligned} \tag{4.9}$$

To calculate according to the variational principle, we use the familiar trial function [5,16]

$$\begin{aligned} &\Psi_{He}(\vec{r}_1, \vec{r}_2) = \frac{Z'^3}{\pi} e^{-Z'(\vec{r}_1 + \vec{r}_2)} , \\ &\mathcal{E}(Z') \equiv \langle H_{He} \rangle = Z'^2 - 2 2 ' 2 + \frac{5}{8} Z' , \\ &\frac{\delta \mathcal{E}}{\delta Z'} = 0 ; \quad Z' = Z - \frac{5}{16} , \\ &\mathcal{E} = E = -\left(Z - \frac{5}{16} \right)^2 . \end{aligned} \tag{4.10}$$

The twoelectron density of this atom is simply

$$\rho_{He_2}(\vec{r}) = 2 \frac{Z'^3}{\pi} e^{-2Z'r} . \tag{4.11}$$

The one-electron density has two cases.

Case IIIa: Perturbed Second Electron

If the one-electron density is chosen to be

$$\rho_{He_1}(\vec{r}) = \frac{Z'^3}{\pi} e^{-2Z'r} , \tag{4.12a}$$

from (3.9) the frontier function becomes

$$\begin{aligned} f_a(\vec{r}) &= \frac{\rho_{He_2} - \rho_{He_1}}{2-1} \\ &= \frac{Z'^3}{\pi} e^{-2Z'r} = \frac{\rho_{He_2}}{2} . \end{aligned} \tag{4.13a}$$

Here we have the perturbed case but with two one-electron systems in a two-body configuration. This consideration is particularly useful as the electron in the state (4.12a) is removed from the helium-like atom.

Case IIIb: Unperturbed Second Electron

When the one-electron configuration is in the unperturbed state (4.2), then the one-electron density is chosen to be

$$\rho_{He_1^0}(\vec{r}) = \frac{Z^3}{\pi} e^{-2Zr}, \tag{4.12b}$$

and from (3.9) the frontier function becomes

$$\begin{aligned} f_b(\vec{r}) &= \frac{\rho_{He_2} - \rho_{He_1^0}}{2-1} \\ &= \frac{2Z'^3}{\pi} e^{-2Z'r} - \frac{Z^3}{\pi} e^{-2Zr} \\ &\neq \frac{\rho_{He_1}}{1} \text{ or } \frac{\rho_{He_2}}{2}. \end{aligned} \tag{4.13b}$$

This consideration is useful for a “stand-by” electron in the state (4.12b) being added to a hydrogen-like atom to form a helium-like atom in the state (4.11), conceptually and mathematically. Here we have the dynamical calculation of the two-electron problem. Three points are notable here. (i) Applications of (3.9) in Cases *II and III* above are for discrete variations of particle numbers. (ii) The perturbed V_{ee} influences the decision of choice of the one-electron density but not the forms of the wave function. (iii) Because the electric potential is kept constant for one- and two-electron cases, it is a dynamical case. When it is one-electron case, the electron is in one quantum state. As the second electron is added, a quantum-mechanical calculation gives the system a two-electron state. If we separate out the first electron state, we find that the state of this first electron is altered or its distribution is rearranged. We call this condition rearrangement of the first electron. The second electron is also changed its state in general, that may be considered as a kind of inelastic collision due to the distribution rearrangement even if its energy is conserved for this second electron. This point is shown clearly in Cases *V and VI* below.

Case IV: Ergodic Variation of Particle Number

To recover from the failure of (3.9) in Case *IIb* above, we consider. continuous variations of electron numbers ergodically. We rewrite the density from (4.11) to

$$\rho_{He_2}(\vec{r}) = N \frac{Z'^3}{\pi} e^{-2Z'r}. \tag{4.14}$$

Here for helium-like atoms N = 2, the same as in (4.11). In (4.14), N is considered as a continuous variable. Thus exactly from (3.9) we find

$$\begin{aligned} f_c(\vec{r}) &= \left(\frac{\delta \rho}{\delta N}\right)_v \\ &= \frac{Z'^3}{\pi} e^{-2Z'r} = \frac{\rho_{He_1}}{1} \text{ or } \frac{\rho_{He_2}}{2}. \end{aligned} \tag{4.15}$$

Hence we have a typical many-body treatment of the problem in an ergodic sense.

In conclusion from several cases discussed above for one-atom systems, we obtain, except for Case IIIb, the frontier function in general

$$f(F) = \frac{\rho(\vec{r})}{N}, \tag{4.16}$$

which is a function of $\vec{r}$ possessing a functional independency of N and ρ from (3.9) and (4.16), i.e. an arithmetic average independent on the electron number. We need not invoke hardness, the second variation of the energy functional. In these systems, dynamical behaviour of the frontier function in a physical system is the same as those of the average local density per single electron, in turn, the same as those of the local density of states of the electron. For example in semiconductor physics, the existence of the density of states means possibilities of accumulation of electrons or holes locally. According to the principle of maximum hardness [15] or the HSAB-principle [9], we gain much insight into this point.

Case *V: Transfers between Two Atoms*

We examine the two-atom case. In physics, this case represents the brief transition state in a collision. Considering collision of two hydrogen-like atoms, we have H(Z_1)-H(Z_2) at a reasonable distance $|\vec{R}|$ reacting similarly to the case given in (2.4); we compare

$$\begin{cases} H(Z_1) + H(Z_2) + \Delta E_1 \rightarrow H(Z_1)^{\delta+} H(Z_2)^{\delta-}, \\ H(Z_1) + H(Z_2) + \Delta E_2 \rightarrow H(Z_1)^{\delta-} H(Z_2)^{\delta+}, \end{cases} \tag{4.17}$$

and obtain from (2.3) and (2.4),

$$\Delta E_1 = \delta[I(1) - A(2)],$$

$$\Delta E_2 = \delta[I(2) - A(1)];$$

$$\Delta E_1 - \Delta E_2 = 2\delta[\chi(1) - \chi(2)] = 2\delta[\mu(2) - \mu(1)].$$

As energies of these hydrogen-like atoms are

$$E(Z_1) = -\frac{Z_1^2}{2}; \qquad E(Z_2) = -\frac{Z_2^2}{2},$$

we have $\mu(1) < \mu(2)$ if $Z_1 > Z_2$. In this case, reaction 2 is favored so that we have the product $H(Z_1)^{\delta-}H(Z_2)^{\delta+}$. During this collision, we expect to have ET that is our present subject.

To calculate the frontier function for continuous transfer at constant v as required by (3.9), we have densities for the two separate atoms respectively before and after the reaction as

$$\begin{aligned} \rho_5^i(1,\vec{r}) &= |\Psi_0(Z_1,r)|^2, \\ \rho_5^i(2,\vec{r}) &= |\Psi_0(Z_2,|\vec{r}-\vec{R}|)|^2, \\ \rho_5^f(1,\vec{r}) &= (1+\delta)\left|\Psi_0\left(Z_{eff} = Z_1 - \frac{5}{16}, r\right)\right|^2, \\ \rho_5^f(2,\vec{r}) &= (1-\delta)|\Psi_0(Z_2,|\vec{r}-\vec{R}|)|^2, \end{aligned} \tag{4.18}$$

in which the effective charge in the ground state of atom 1 is altered to the screening one, Z_{eff}, because more than one electron occupy the same orbital. As required according to constant v, the expression given in (4.18) is more precise than conventional molecular-orbital results. Therefore from (3.9), we obtain the frontier functions

$$\begin{aligned} f_5(1,\vec{r}) &= \frac{1+\delta}{\delta}\left|\Psi_0\left(Z_1 - \frac{5}{16}, r\right)\right|^2 - \frac{1}{\delta}|\Psi_0(Z_1,r)|^2 \\ &= \frac{1+\delta}{\delta}\frac{Z_{eff}^3}{\pi}e^{-2Z_{eff}r} - \frac{1}{\delta}\frac{Z_1^3}{\pi}e^{-2Z_1 r} \neq \frac{\rho}{N}, \end{aligned} \tag{4.19}$$

$$f_5(2,\vec{r}) = \frac{Z_2^3}{\pi}e^{-2Z_2|\vec{r}-\vec{R}|}. \tag{4.20}$$

If we consider for the integer number transfer (if it exists), 6 = 1, the initial densities ρ_5^i are the same as those given in (4.18). The final densities become

$$\begin{aligned} \rho_{51}^f(1,\vec{r}) &= 2\left|\Psi_0\left(Z_1 - \frac{5}{16}, \vec{r}\right)\right|^2, \\ \rho_{51}^f(2,\vec{r}) &= 0. \end{aligned} \tag{4.21}$$

Here we may consider a quantum jump to occur. Then frontier functions are the same as those given in (4.19) and (4.20) with $\delta = 1$.

To calculate the ET number for a hydrogen-like atom of nuclear charge Z, we have from (4.10), (2.3), and (2.5a),

$$\begin{aligned} I(Z) &= \frac{Z^2}{2}, \quad A(Z) = \left(Z - \frac{5}{16}\right)^2 - \frac{Z^2}{2}; \\ \mu(Z) &= -\frac{I+A}{2} = -\frac{1}{2}\left(Z - \frac{5}{16}\right)^2, \\ \eta(Z) &= \frac{1}{2}(I-A) = \frac{5}{16}\left(Z - \frac{5}{32}\right). \end{aligned} \tag{4.22}$$

According to (2.8), we have the ET number

$$\delta_5 = \frac{P(2) - \mu(1)}{2(\eta(1)+\eta(2))} = \frac{(Z_1 - Z_2)(Z_1 + Z_2 - \frac{5}{8})}{\frac{5}{4}(Z_1 + Z_2 - \frac{5}{16})} \tag{4.23}$$

which is not in general an integer. There is clearly no covalent bonding, as seen from (4.23) in the limit $Z_2 \rightarrow Z_1$. In the calculations we used the hardness and apply for integral Z. There exist cases of many hydrogen-like atoms of large Z. To calculate δ_5, we choose $Z_1 = 11$ (Na) and $Z_2 = 10$ (Ne). The calculated ET number during the collision is

$$\delta_5(11, 10) = 0.79.$$

Hence most electrons accumulate on the first atom with a tendency to neutralize materials, as expected. We occasionally expect to have fractional Z, e.g. $5/16 < Z_1 + Z_2 < 5/8$ in (4.23) above. It becomes realistic in the Coulomb blockade problem in cases of artificial atoms in which nuclear charges are controlled by gate voltages and can be fractional [2]. Then how to determine the ET number and what is η become interesting. Further, from (4.18) or (4.20) we have more charge accumulating at the first atom which can be explained as there is an available vacant level. Here we have less charge at the second atom; it is a pure ET effect.

It is natural to consider the configuration of the product $H(Z_1)^{\delta-}H(Z_2)^{\delta+}$ as a molecule-like system and as a whole. This situation is obvious because densities are additive. To calculate the frontier function for continuous transfer at constant v as required by (3.9), we have total densities for the two separate atoms before and after the reaction as

$$\begin{aligned} \rho_5^i(\vec{r}) &= \rho_5^i(1, \vec{r}) + \rho_5^i(2, \vec{r}), \\ \rho_5^f(\vec{r}) &= \rho_5^f(1, \vec{r}) \ \mathrm{t} \ \rho_5^f(2, \vec{r}). \end{aligned} \tag{4.24}$$

According to (3.9), the variation of the number δN is undefined. If we assume that the frontier function is also additive, we obtain a function

$$\begin{aligned} f_5(\vec{r}) &= f_5(1, \vec{r}) + f_5(2, \vec{r}) \\ &= \frac{1+\delta}{\delta} \frac{Z_{eff}^3}{\pi} e^{-2Z_{eff}r} - \frac{1}{\delta} \frac{Z_1^3}{\pi} e^{-2Z_1 r} + \frac{Z_2^3}{\pi} e^{-2Z_2|\vec{r}-\vec{R}|} \\ &\neq \frac{\rho}{N}. \end{aligned} \tag{4.25}$$

In this result, the normalization of $f_5(\vec{r})$ differs from that of $f_5(1, \vec{r})$ or $f_5(2, \vec{r})$. In conclusion, for the above molecule-like system that is formed from two atoms, the frontier function cannot be obtained by summation of its components. Therefore frontier *functions* are not additive. The usefulness of this frontier function is thus restricted.

Case VI: He-H Transfer

By analogy with ***Case V*** above, we consider a hydrogen-like atom colliding with a helium-like ion $\mathrm{Li}^+ (Z = 3)$ treated in the Heisenberg method [5] with a ground state $1s^2 2s$. The initial densities for these two atoms are given as

$$\begin{aligned} \rho_6^i(1,\vec{r}) &= 2\frac{Z'^3}{\pi}\, e^{-2Z'r} + 0\cdot\frac{Z''^3}{\pi}e^{-2Z''r}, \\ \rho_6^i(2,\vec{r}) &= |\Psi_0(Z_2,|\vec{r}-\vec{R}|)|^2, \qquad (4.26) \\ Z' &= 3-\frac{5}{16} = 2.6875, \end{aligned}$$

in which hydrogen-like wave functions are used as treated in Ref. [5]. The two electrons in Li^+ have the same screening charge as that in (4.10). In Ref. [5], in atomic units, we have for the third electron in Li and for the hydrogen-like atom,

$$\begin{aligned} I_3 &= 3.37, \qquad & A_3 &= 0.2; \\ I_2 &= \frac{Z_2^2}{2}, \qquad & A_2 &= \left(Z_2-\frac{5}{16}\right)^2 - \frac{Z_2^2}{2}. \end{aligned} \qquad (4.27)$$

We find two cases for two ranges of values of Z_2.

Case VIa: $Z_2 > 3,\ \mu_1 > \mu_2$

For one example, we take $Z_2 = 4$, i.e. a Li^+-Be^{3+} collision. In this case, the electron is transferred from Li^+ to Be^{3+}. Because the ionization energy of Li^+ is that of the second electron, thus of a helium-like atom, we have

$$I_1 = \frac{1}{2}\left(3-\frac{5}{16}\right)^2 = 3.61,$$

instead of I_3 given in (4.27). The chemical potentials and ionization energies are

$$\begin{aligned} \mu_1 &= -1.91, \qquad \eta_1 = 1.71; \\ \mu_2 &= -\frac{1}{2}\left(Z_2-\frac{5}{16}\right)^2 = -6.80, \qquad \eta_2 = \frac{5}{16}\left(Z_2-\frac{5}{32}\right) = 1.20. \end{aligned} \qquad (4.28)$$

The ET number is then

$$\delta_{6+} = 0.84, \qquad (4.29)$$

which is ET in this collision to form a molecule-like system. After the collision, we have the same effects as if there were a molecular detachment dissociation. Thus the final densities and frontier functions are obtained as

$$\begin{aligned} \rho_{6a}^f(1,\vec{r}) &= \left(1-\frac{\delta_{6+}}{2}\right)2\frac{Z'^3}{\pi}e^{-2Z'r}, \\ \rho_{6a}^f(2,\vec{r}) &= (1+\delta_{6+})\left|\Psi_0\left(Z_{eff} = Z_2-\frac{5}{16},|\vec{r}-\vec{R}|\right)\right|^2. \end{aligned} \qquad (4.30a)$$

$$\begin{aligned} f_{6a}(1,\vec{r}) &= \frac{Z'^3}{\pi}e^{-2Z'r}, \\ f_{6a}(2,\vec{r}) &= \frac{1+\delta_{6+}}{\delta_{6+}}\left|\Psi_0\left(Z_2-\frac{5}{16},|\vec{r}-\vec{R}|\right)\right|^2 - \frac{1}{\delta_{6+}}|\Psi_0(Z_2,|\vec{r}-\vec{R}|)|^2. \end{aligned} \qquad (4.30b)$$

The frontier function was originally understood to have contributions from the highest occupied atomic orbital (HOAO) for atom 1 and from the lowest unoccupied atomic orbital (LUAO) for atom 2. Here it has a large contribution from the unperturbed state also, i.e. the last term in (4.30b) which is not even a ‘ core ’ or valence orbital. We must try to understand further, particularly from ideas about the density of states.

Case *VIb:* $Z_2 \leq 3,\ \mu_1 < \mu_2$

In this case, the electron is transferred from atom 2 to Li^+. For only three cases, Z_2 = 1, to 3, we obtain ET numbers as

$$\begin{aligned} \delta_{6-}(Z_2 &= 3) = 0.019, \\ \delta_{6-}(Z_2 &= 2) = 0.086, \\ \delta_{6-}(Z_2 &= 1) = 0.42. \end{aligned} \tag{4.31}$$

According to the result for Z_2 = 3 above, i.e. Li^+-Li^{2+} collision, the effect of ET that is due to the difference of chemical potential is not subjected to the electric symmetry of charges. It is not of electromagnetic origin. This is one purpose for which we present this review. The final densities and frontier functions are obtained as

$$\begin{aligned} \rho^f_{6b}(1,\vec{r}) &= 2\frac{Z'^3_1}{\pi}e^{-2Z'_1 r} + \delta_{6-}\frac{Z''^3}{\pi}e^{-2Z'' r}, \\ \rho^f_{6b}(2,\vec{r}) &= (1-\delta_{6-})|\Psi_0(Z_2,|\vec{r}-\vec{R}|)|^2. \end{aligned} \tag{4.32a}$$

$$\begin{aligned} f_{6b}(1,\vec{r}) &= \frac{2}{\delta_{6-}}\left(\frac{Z'^3_1}{\pi}e^{-2Z'_1 r} - \frac{Z'^3}{\pi}e^{-2Z' r}\right) + \frac{Z''^3}{\pi}e^{-2Z'' r}, \\ f_{6b}(2,\vec{r}) &= |\Psi_0(Z_2,|\vec{r}-\vec{R}|)|^2. \end{aligned} \tag{4.32b}$$

Because more than two electrons exist in the final state of the first atom, we have Z'_1 = 2.59699 from Ref. [5] instead of Z' = 2.6875 in (4.26) above. This change in $Z' \Rightarrow Z'_1$ is concluded as the rearrangement of the “ core state ”. The frontier functions have contributions from the (perturbed) HOAO of atom 1 with the perturbed term from the “ core state ” rearrangement, and from the (unperturbed) LUAO of atom 2.

V. SUMMARY

In simple quantum systems of Rydberg atom collisions, we examined electron transfer. The occurrence of a process of this kind is due to the chemical potential variations or differences, *independent of electromagnetic interactions and symmetries.* The magnitude of this transfer is given in (2.8). The main quantity of interest is the frontier function. One expression of this function is given in (3.16) that shows the distribution of the local density of states. In turn, this function shows the possibility of accumulation of electrons spatially. This point is one of great interest in many branches of physics; e.g. semiconductor physics is one of them. Furthermore, in semicondutor considerations, we apply such conjecture by intuition. The theory shown in this review confirms that thought of this kind is correct.

In our investigation of Rydberg atom systems, for one-atom systems, the frontier function represents the electron density shared per electron, i.e. ρ/N in (4.16). We considered only up to helium-like atoms that have only orbitals in one shell. It shows that the larger frontier function accumulates more electrons. The calculations are essentially for discrete alterations of numbers of elections, AN = 1. The electron distributions are derived from perturbed (dynamic), unperturbed or ergodic treatment of quantum states. The nature of the added electron that we consider in ΔN is relevant according to the case that it is added to the system (as an unperturbed electron) or removed from the system (as in a perturbed state). For two-atom systems, *Cases V and VI,* the physical situations are complicated. First orbital-occupation concepts of the so-clled frontier orbitals are essential happened. Therefore the so-called HOAO and LUAO are useful concepts. However the "soft likes soft" in the HSAB-principle is interesting and the soft-soft interaction is due to the covalent effect that comes from electromagnetic considerations as also treated in molecular physics. In this review, hard-hard interactions induce ET effects that is not the result of e.m. interactions as shown explicitly in (4.23) and (4.31) above. Still the rearrangement effect of existing electrons should be considered. The conclusion is also applicable to solids. The similarities between various occupation-possibilities of charges, and the strengths of the soft-soft and hard-hard interactions should be considered severely. Actually the rearrangement in solids is a difficult and unsolved problem in physics [17]. Its influences on the possibilities of occupations of electrons require further investigation. Recent report on possible transitions in Rydberg atoms including ET effects can be found in Ref. [18].

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