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REGULAR ARTICLE

On the electronegativity nonlocality paradox

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Abstract The electronegativity equalization principle states that, in its ground state, the electronegativity of every component in a system is the same. A paradox then arises: molecular fragments that are very far apart must still have the same electronegativity, which seems to contradict the common assumption that spatially separated molecular species can be described independently. Density-functional theory provides the tools needed to analyze this paradox at a fundamental level, and a resolution is found from the properties of the exact Hohenberg–Kohn functional. Specifically, there is no paradox because the electronegativity is not uniquely defined for separated systems. Instead, there is an "apparent electronegativity" that preserves locality. This may have implications for the treatment of charge-transfer excited states. A model for the energy as a function of the number of electrons is also presented. This model gives some insight into the utility of the grand canonical ensemble formulation (at nonzero temperature) and, unlike most previous models, this model recovers the appropriate behavior in the limits of infinitely separated and/or weakly interacting subsystems.

Keywords Electronegativity equalization · Electron transfer · Conceptual density-functional theory · Chemical potential · Excited states · Fractional electron number

1 Introduction

In 1978, Parr et al. [1] published a paper entitled "Electronegativity: the density-functional viewpoint" which defined the electronic chemical potential as the derivative of the energy with respect to the number of electrons at fixed molecular geometry [1],[1]

$$\mu \equiv \left(\frac{\partial E}{\partial N}\right)_{v(\mathbf{r})}. \tag{1}$$

Then, following Itzkowski and Margrave [2] they defined the electronegativity as the additive inverse of the chemical potential [1],

$$\chi = -\mu. \tag{2}$$

Using the Hohenberg–Kohn theorems, Parr et al. [1] (hereafter PDLP) showed that the variational principle for the energy implies that the electronic chemical potential is constant in the ground state of a molecule, thereby deriving Sanderson's electronegativity equalization principle [3,4]. This demonstrated that density-functional theory (DFT) provides a natural language for discussing chemical reactions and chemical reactivity [5–8] and stimulated further work on using DFT to elucidate important chemical concepts like regio selectivity [9–11] hard/soft acid/base theory [12–19] aromaticity [20,21], electrophilicity [22–24], and nucleofugality [6,25–27]. Even more impressively, DFT-based methodology has led to entirely new chemical concepts, notably the maximum hardness principle [28–32] and the recently proposed external-potential-based chemical reactivity indicators [33–37].

Many outstanding issues remaining in the treatment of chemical reactivity, but this paper will concentrate on the

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[1] Most electronic structure calculations are performed at zero temperature, where Eq. (1) is rigorously correct. In a finite temperature calculation, the chemical potential is the derivative of the free energy. The entropic contribution to the free energy is usually negligible, however, because electronic energy level spacings typically much larger than the thermal energies of interest to chemists. (Boltzmann's constant is 3.17 10-6 Hartrees per degree Kelvin!) So Eq. (1) remains an excellent approximation even for finite temperature DFT.

very basic foundations of conceptual density functional theory and, in particular, a fundamental problem related to electronegativity equalization. Suppose two atoms—say, Cesium and Fluorine—are separated by a distance R, which we take to approach infinity. The atoms are not interacting with one another and so they may be assumed to act independently. The electronegativity equalization principle indicates that the electronegativity of the individual atoms is equal to a constant that depends on the *entire* system, and not just the individual atoms. For example, adopting the Mulliken approximation to the electronegativity, the electron affinity for this system is that of Fluorine, and the ionization potential is that of Cesium, and so

$$\underbrace{\lim}_{R\to\infty} \chi_{\text{Mulliken}} = \frac{I_{\text{Cs}} + A_F}{2}. \tag{3}$$

The electronegativity of atoms and molecules, then, is subject to a locality paradox[2]. the electronegativity of the atom is given by a common value characteristic of the system even if all the other components of the system are infinitely far away.

Studying this paradox is the purpose of this paper. Since the chemical potential is related to the dependence of the energy on the number of electrons, Sect. 2 discusses how the energy may be defined for molecules with noninteger electron number. Section 3 is loosely based on PDLP and provides a precise mathematical statement of the chemical potential equalization principle in normal (i.e., nondissociated) molecules. This review provides the key mathematical tools for Sect. 4, where the distance between the systems goes to infinity. Sect. 5 explains why there is no chemical potential equalization locality paradox and discusses the implications for charge transfer excited states. Section 6 concludes.

2 The energy as a function of the number of electrons

Because a function that is defined only on the integers is not differentiable, the definition of the chemical potential in Eq. (1) requires defining the energy for noninteger numbers of electrons. For an isolated molecular system at zero temperature, the definition of the energy as a function of the number of electrons is imposed by the observation that the energy is a size consistent property of the system [38,39]. In that case, the energy is a piecewise linear function of the number of electrons [38–41].

$$E[v;N] = (\lceil N\rceil - N)E[v;\lfloor N\rfloor] + (N - \lfloor N\rfloor)E[v;\lceil N\rceil] \tag{4}$$

where $\lfloor N\rfloor$ is the "floor" function, [3] which is the largest integer that is less than or equal to N and $\lceil N\rceil = \lfloor N\rfloor + 1$ is the "ceiling" function, which is the next integer greater than N. This energy expression is not differentiable for integer numbers of electrons, but the one-sided derivatives (derivatives from above and below) still exist.

Sometimes it is more convenient to use energy functionals that are differentiable functions of the number of electrons. Such representations are appropriate, for example, for reactions in solution, where the solvent molecules provide a "reservoir" of electrons with a set chemical potential. At a formal level, it is clear how one can achieve this: one defines the "reduced" density matrix for the molecule in the "bath" of electrons and the "effective potential" provided by its surroundings [18,19],

$$\begin{aligned} D_{\text{mol.}}\left(\mathbf{x}_1,\ldots;\mathbf{x}'_1,\ldots\right) &= p_0\,|0\rangle\,\langle 0| + p_1 D_1\left(\mathbf{x}_1;\mathbf{x}'_1\right) \\ &\quad + p_2 D_2\left(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}'_1,\mathbf{x}'_2\right) + \cdots \end{aligned} \tag{5}$$

where $|0\rangle$ denotes the vacuum, p_k denotes the probability of observing exactly k-electrons in the molecule, and the k-electron density matrix describes the k-electron state of the molecule,

$$\begin{aligned} &D_k\left(\mathbf{x}_1,\ldots,\mathbf{x}_k;\mathbf{x}'_1,\ldots,\mathbf{x}'_k\right) \\ &\quad = \sum_i n_i \psi_i(\mathbf{x}_1,\ldots,\mathbf{x}_k)\psi_i^*\left(\mathbf{x}'_1,\ldots,\mathbf{x}'_k\right) \\ &\quad\quad \sum_i n_i = 1;\, 0 \le n_i \le 1;\, \left\langle\psi_j\,|\psi_i\right\rangle = \delta_{ij} \end{aligned} \tag{6}$$

Both $\{p_k\}$ and $\{D_k\}$ depend on the molecule's surroundings.

It is very difficult to evaluate Eq. (5). First of all, one must compute the complete density matrix for the *entire* system (molecule + surroundings). Then one needs to partition the system's density matrix into the density matrices of the molecule and its surroundings. (Symbolically, one needs a reasonable method for performing the decomposition: $\Gamma_{\text{mol.+ bath}} = \Gamma_{\text{mol.}} \hat{} \Gamma_{\text{bath}}$, where $\hat{}$ is the antisymmetric "Fock space" tensor product.) There is an inherent arbitrariness in this construction because there are many reasonable procedures for performing the partitioning [42]. In particularly, there are approaches based on a Hilbert-space analysis [43–48] and approaches based on spatial partitioning schemes [49–52].

Approximations with the general form of Eq. (5) are already known. Cohen has used a grand-canonical ensemble approach in his method based on the "reactivity potential [53,54]. (His target is an exact approach, while in this paper the goal is for a conceptual and "pragmatic" approach.) For our purposes, however, it is useful to see how this sort of approximation has previously been used in the context of "conventional" computational chemistry. For example, an

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[2] The author was introduced to this paradox by Max Berkowitz, who referred to it as the "EPR paradox" of density functional reactivity theory.

[3] This is evaluated by truncating the decimal representation of N.

approximation like Eq. (5) underlies the quantum mechanics/molecular mechanics hybrid method [55–59] In that case, the number of electrons in the molecule is fixed (i.e., the only nonzero term in Eq. (5) is the term with $k = N_{\text{mol.}}$) and the only effect of the molecule's surroundings is to deform (i.e., polarize) the molecular wavefunction. That is,

$$\begin{aligned} &D_{\text{mol.}}^{\text{QM/MM}}\left(\mathbf{x}_1,\ldots,\mathbf{x}_{N_{\text{mol.}}};\mathbf{x}'_1,\ldots,\mathbf{x}'_{N_{\text{mol.}}}\right) \\ &\quad = \left|\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};N_{\text{mol.}}\right]\right\rangle\left\langle\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};N_{\text{mol.}}\right]\right| \end{aligned} \tag{7}$$

where $\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};N_{\text{mol.}}\right]$ is the ground-state wavefunction of the molecule in the "effective external potential" defined by the atomic nuclei in the molecule ($v_{\text{QM}}(\mathbf{r})$) and effective external potential from the molecule's surroundings ($v_{\text{MM}}(\mathbf{r})$) [34,51]. $v_{\text{MM}}(\mathbf{r})$ is commonly approximated by the electrostatic potential of the molecule's surroundings.

Moving beyond this simple approximation requires determining the density matrix of the entire system. The density matrix for the molecule could then be approximated by the following procedure

$$\begin{aligned} &D_{\text{mol.}}^{\text{g.s.}}\left(\mathbf{x}_1,\ldots,\mathbf{x}_{N_{\text{mol.}}};\mathbf{x}'_1,\ldots,\mathbf{x}'_{N_{\text{mol.}}}\right) \\ &= \sum_{k=0}^{\infty}\left\{\begin{aligned} &\left\langle\Psi_{\text{mol. + bath}}\right|\ \left|\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle \\ &\times\ \left\langle\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right|\ \left|\Psi_{\text{mol. + bath}}\right\rangle \\ &\times\left|\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle\left\langle\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right| \end{aligned}\right\} \quad (8) \\ &= \sum_{k=0}^{\infty}\left\{\begin{aligned} &\left(\text{Tr}\left[\Gamma_{\text{mol. + bath}}\times\left|\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle\right.\right. \\ &\quad\times\ \left.\left.\left\langle\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right|\right]\right) \\ &\quad\times\left(\left|\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle\left\langle\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right|\right) \end{aligned}\right\} \end{aligned}$$

$$\begin{aligned} &D_{\text{mol.}}^{\text{g.s. + e.s.}}\left(\mathbf{x}_1,\ldots,\mathbf{x}_{N_{\text{mol.}}};\mathbf{x}'_1,\ldots,\mathbf{x}'_{N_{\text{mol.}}}\right) \\ &= \sum_{k=0}^{\infty}\sum_{m=0}^{K}\sum_{n=0}^{K}\left\{\begin{aligned} &\left(\text{Tr}\left[\Gamma_{\text{mol. + bath}}\right.\right. \\ &\times\left.\left.\left|\Psi_m\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle\left\langle\Psi_n\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right|\right]\right) \\ &\left(\left|\Psi_n\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle\left\langle\Psi_m\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right|\right) \end{aligned}\right\} \end{aligned} \tag{9}$$

Only a few excited states can be included in this representation because highly excited states of the "molecule" will be substantially delocalized onto the molecule's surroundings. This problem could be avoided if a spatial partitioning was used instead of the Hilbert-space partitioning.

The refinements in Eqs. (8) and (9) are probably computationally impossible. One can argue, however, that the main effect is the "polarization" of the molecule by its surroundings. From the perspective of perturbation theory, polarizing the molecule mixes excited state contributions into ground state wavefunction and raises the energy of the molecule. (The total energy decreases, however, because the attractive interactions of the polarized molecule with its surroundings are twice as large as the energy destabilization due to the deformation.) Heating the molecule also causes excited electronic states to be mixed with the ground state, though in that case the mixture of excited states with the ground states is incoherent (giving a "mixed state") instead of coherent (giving a "superposition state"). This suggests modeling the molecular surroundings as a "heat bath" with an effective temperature and an effective electronic chemical potential,

$$\begin{aligned} &D_{\text{mol.}}^{\beta_k^{eff}}\left(\mathbf{x}_1,\ldots,\mathbf{x}_{N_{\text{mol.}}};\mathbf{x}'_1,\ldots,\mathbf{x}'_{N_{\text{mol.}}}\right) \\ &= \frac{\sum\limits_{k=0}^{\infty}\left\{e^{-\beta_k^{eff}\left(E_{\text{mol.}}\left[v_{\text{QM}}+v_{\text{MM}},k\right]-\mu k\right)}\left(\left|\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle\left\langle\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right|\right)\right\}}{\sum\limits_{l=0}^{\infty}e^{-\beta_k^{eff}\left(E_{\text{mol.}}\left[v_{\text{QM}}+v_{\text{MM}},k\right]-\mu k\right)}} \end{aligned} \tag{10}$$

Here $\Psi_{\text{mol + bath}}$ denotes the wavefunction of the system *and* its surroundings. Since this problem is properly treated within the framework of statistical mechanics, however, it is better to consider the density matrix of the entire system, $\Gamma_{\text{mol. + bath}}$, as in the second equality. Notice how the QM/MM results are leveraged to make this simple representation possible. This is not an exact procedure and, in general, one would need to include more than just the ground state of the QM/MM system. Denoting the excited states of the QM/MM system as $\Psi_n\left[v_{\text{QM}}+v_{\text{MM}};N_{\text{mol.}}\right]$, a more accurate representation would be

The effective temperature models how strongly the system and its surroundings interact and, if it is chosen appropriately, should give an adequate approximation to the true coupling between the molecule and its environment:

$$\begin{aligned} &\frac{e^{-\beta_k^{\text{eff}}\left(E_{\text{mol.}}\left[v_{\text{QM}}+v_{\text{MM}},k\right]-\mu k\right)}}{\sum\limits_{l=0}^{\infty}e^{-\beta_k^{\text{eff}}\left(E_{\text{mol.}}\left[v_{\text{QM}}+v_{\text{MM}},k\right]-\mu k\right)}} \\ &\quad\approx \text{Tr}\left[\Gamma_{\text{mol. + bath}}\left|\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right\rangle\right. \\ &\qquad\times\left.\left\langle\Psi_0\left[v_{\text{QM}}+v_{\text{MM}};k\right]\right|\right] \end{aligned} \tag{11}$$

In keeping with the preceding discussion, the effective temperature can be approximated by the requiring that the "amount of excitation energy due to the effective temperature" matches the "amount of excitation energy due to molecular polarization." The chemical potential, μ, that enters into Eq. (10) is used to ensure that the number of electrons in the molecule matches the number of electrons in the molecule obtained from population analysis techniques on the density matrix of the entire system (molecule + bath). Notice that the effective temperature will naturally decrease to zero if the molecule interacts very weakly with its surroundings; for example, if a two-state model is used to evaluate the effective temperature, one has

$$\beta_k^{\text{eff}} = \frac{1}{\eta_k} \ln\left(\frac{\eta_k}{E_k^{(\text{polrztn})}} - 1 \right) \tag{12}$$

where $E_k^{(\text{polrztn})}$ is the increase in the energy of the k-electron molecule due to polarization by it surroundings and η_k is the band gap for the k-electron molecule.

Even Eq. (10) is often too complicated for practical utility. If one is interested in the "generic" reactivity profile of a molecule in solution, one often models the solution with a continuum solvation model or even neglects it altogether. If the molecular surroundings are neglected altogether, then β_k^{eff} becomes an empirical constant, where a large value of β_k^{eff} (low temperature) would be appropriate for a molecule that interacts weakly with its environment (e.g., a molecule in an Argon matrix) while a small value of β_k^{eff} (high temperature) would be appropriate for a molecule that interacts strongly with its environment (e.g., a molecule dissolved in an ionic liquid). If one further assumes that β_k^{eff} does not depend on the number of electrons, then one recovers the grand-canonical ensemble originally proposed by Gyftopoulos and Hatsopoulos, [60] extended by Perdew, Parr, Levy, and Balduz, [40] and later elaborated upon by Chan [61],

$$\begin{aligned} & D_{\text{mol.}}^{\beta^{\text{eff}}}\left(\mathbf{x}_1, \ldots, \mathbf{x}_{N_{\text{mol.}}}; \mathbf{x}'_1, \ldots, \mathbf{x}'_{N_{\text{mol.}}}\right) \\ & \quad = \frac{\sum\limits_{k=0}^{\infty} \left\{ e^{-\beta^{\text{eff}}\left(E_{\text{mol.}}\left[v_{\text{QM}}, k\right] - \mu k\right)} \left(\left|\Psi_0\left[v_{\text{QM}}; k\right]\right\rangle \left\langle \Psi_0\left[v_{\text{QM}}; k\right]\right| \right) \right\}}{\sum\limits_{l=0}^{\infty} e^{-\beta^{\text{eff}}\left(E_{\text{mol.}}\left[v_{\text{QM}}, k\right] - \mu k\right)}}. \end{aligned} \tag{13}$$

Equation (13) is very commonly used when one wishes to have a smooth and differentiable form for the energy as a function of the number of electrons [5]. It is a sensible approximation insofar as it can be derived by successive approximations from the more accurate and rigorous form in Eq. (9).

Once the density matrix is determined, the energy as a function of the number of electrons can be constructed. One writes the number operator and the energy operator as integral kernels,

$$\begin{aligned} \hat{N}_k &= \sum_{n=0}^{\infty} \left|\Psi_n\left[v_{\text{QM}} + v_{\text{MM}}; k\right]\right\rangle \left\langle \Psi_n\left[v_{\text{QM}} + v_{\text{MM}}; k\right]\right| \\ \hat{H}_k &= \sum_{n=0}^{\infty} \left|\Psi_n\left[v_{\text{QM}} + v_{\text{MM}}; k\right]\right\rangle \\ & \qquad \times E_{\text{mol.},n}\left[v_{\text{QM}} + v_{\text{MM}}; k\right] \left\langle \Psi_n\left[v_{\text{QM}} + v_{\text{MM}}; k\right]\right| \end{aligned} \tag{14}$$

and then evaluates the total energy and the total number of electrons as

$$\begin{aligned} N\left[v_{\text{QM}}, \mu\right] &= \text{Tr}\left[\left(\sum_{k=0}^{\infty} \hat{N}_k \right) \Gamma_{\text{mol.}} \right] \\ E\left[v_{\text{QM}}, \mu\right] &= \text{Tr}\left[\left(\sum_{k=0}^{\infty} \hat{H}_k \right) \Gamma_{\text{mol.}} \right] \end{aligned} \tag{15}$$

Only the "molecular" external potential and the chemical potentials are variables in these equations; if a QM/MM approach was taken, the MM potential would be determined by the identity of the QM system.

When one takes the limit of weak interactions of the molecule with its surroudings, $\beta^{\text{eff}} \to \infty$ (temperature goes to zero) and one recovers the piecewise linear formula in Eq. (4). Because the piecewise linear function is appropriate for molecules in isolation, it will be the basis of much of the subsequent analysis. The "nonlocality" paradox mentioned in the introduction is intimately related to what happens when molecules dissociate in isolation and there is no paradox when the molecule's surroundings serves as a reservoir of electrons, imposing a single well-defined value on the chemical potential.

3 Chemical potential equalization in ordinary systems

3.1 Functional derivatives

The relationship between density-functional theory and the chemical potential equalization principle hinges on the variational principle for the electron density: the density-functional for the energy,

$$E_v[\rho] = F[\rho] + \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \tag{16}$$

is minimized by the ground state electron density of the N-electron system, $\rho_N(\mathbf{r})$, and it is stationary at this point [62]. In Eq. (16), $F[\rho]$ is the Hohenberg–Kohn functional and $v(\mathbf{r})$ denotes the external potential. For an isolated molecule, the external potential is just the attractive potential from the atomic nuclei.

The Hohenberg-Kohn functional is defined by

$$F[\rho] = E[v; N] - \int \rho(\mathbf{r}) v(\mathbf{r}) d\mathbf{r} \tag{17}$$

for v-representable electron densities. For non-v-representable electron densities, $F[\rho]$ can be defined by constrained search, [63,64] continuity arguments [65], or the Legendre transform [69]

$$F[\rho] = \underbrace{\sup}_{v(\mathbf{r})}\left[E[v;N] - \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r}\right] \tag{18}$$

Valone's density-matrix constrained search, the continuity method, and the Legendre transform all give identical results [65,66].There is also a "dual space" formulation that avoids the v-representability problem altogether [67].

The electronegativity equalization principle is derived by studying how the electronic energy changes in response to changes in electron density. This is accomplished using the functional derivative. The functional derivative of the energy with respect to the electron density, evaluated at the electron density $\rho_0(\mathbf{r})$, is *defined* as the function, $\frac{\delta E_v[\rho_0]}{\delta\rho(\mathbf{r})}$[4], that maps arbitrary infinitesimal changes in the electron density, $\delta\rho(\mathbf{r})$, to the appropriate change in the energy through the formula

$$\begin{aligned} &E_v[\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})] - E_v[\rho_0(\mathbf{r})] \\ &\quad = dE_v[\rho_0] \equiv \int \frac{\delta E_v[\rho_0]}{\delta\rho(\mathbf{r})}\delta\rho(\mathbf{r})d\mathbf{r}. \end{aligned} \tag{19}$$

In Eq. (19), $\frac{\delta E_v[\rho_0]}{\delta\rho(\mathbf{r})}\delta\rho(\mathbf{r})$ must be integrated over all space because $\delta\rho(\mathbf{r})$ is generally nonzero at more than just one point. When a point perturbation, $\delta\rho(\mathbf{r}) = \varepsilon\delta(\mathbf{r}-\mathbf{r}_0)$, is used, the spatial integration in (19) may be omitted and we obtain an alternative definition for the functional derivative:

$$\begin{aligned} \frac{\delta E_v[\rho_0]}{\delta\rho(\mathbf{r}_0)} &\equiv \underbrace{\lim}_{\varepsilon\to 0}\frac{E_v[\rho_0(\mathbf{r}) + \varepsilon\delta(\mathbf{r}-\mathbf{r}_0)] - E_v[\rho_0(\mathbf{r})]}{\varepsilon} \\ &= \left(\frac{\partial E_v[\rho_0(\mathbf{r}) + \varepsilon\delta(\mathbf{r}-\mathbf{r}_0)]}{\partial\varepsilon}\right)\Bigg|_{\varepsilon=0}. \end{aligned} \tag{20}$$

In addition to providing a convenient way to evaluate functional derivatives, (20) provides the basis for an intuitive understanding of functional differentiation: $\frac{\delta E_v[\rho_0]}{\delta\rho(\mathbf{r}_0)}$, *the functional derivative of the energy with respect to the electron density at the point* $\mathbf{r}_0$*, represents the incremental increase in energy due to increasing the electron density,* $\rho_0(\mathbf{r})$*, by a small amount at* $\mathbf{r}_0$.

The definition of the functional derivative is analogous to the definition of the gradient: the gradient of a function at the point $\mathbf{x}_0$, $\nabla f(\mathbf{x}_0)$, is *defined* as the function that maps infinitesimal changes in the argument of the function, $d\mathbf{x}$, to changes in the value of the function according to the formula

$$\begin{aligned} f(\mathbf{x}_0 + d\mathbf{x}) - f(\mathbf{x}_0) &\equiv \nabla f(\mathbf{x}_0)\cdot d\mathbf{x} \\ &= \sum_{i=1}^{d}\frac{\partial f(\mathbf{x})}{\partial x_i}\bigg|_{\mathbf{x}=\mathbf{x}_0} dx_i \end{aligned} \tag{21}$$

The second equality in Eq. (21) breaks the gradient and the change in abscissa into its individual components. A similar form is obtained when the integral in Eq. (19) is expressed as Riemann sum; the functional derivative is an infinite-dimensional analogue of differentiation.

Sometimes a function is non-differentiable: there exists no vector $\nabla f(\mathbf{x}_0)$, that suffices to map every possible choice for $d\mathbf{x}$ to the corresponding change in the functional value, $f(\mathbf{x}) - f(\mathbf{x}_0)$. In this case, the gradient does not exist. In many cases, however, the *directional derivative* still exists: that is, there is a mapping with the form of Eq. (21), but the value of the gradient depends on the direction of the perturbation,

$$f(\mathbf{x}_0 + d\mathbf{x}) - f(\mathbf{x}_0) = \mathcal{D}_{\mathbf{x}_0}[f; d\mathbf{x}] = \frac{\partial f(\mathbf{x}_0 + \varepsilon d\mathbf{x})}{\partial\varepsilon}\bigg|_{\varepsilon=0}. \tag{22}$$

The gradient exists when $\mathcal{D}_{\mathbf{x}_0}[f; d\mathbf{x}]$ is a linear functional of $d\mathbf{x}$.

Similarly, sometimes it is true that the change in the value of a functional depends on the specific choice of the perturbation in a way that cannot be captured by the expression for the functional derivative, (19). In many cases, however, a formula like Eq. (19) can be recovered by allowing the functional derivative to depend on the type of perturbation:

$$\begin{aligned} &E_v[\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})] - E_v[\rho_0(\mathbf{r})] \\ &\quad = \int \delta E_{\rho_0}[\delta\rho; \mathbf{r}]d\mathbf{r} = \frac{\partial E[\rho_0 + \varepsilon\delta\rho]}{\partial\varepsilon}\bigg|_{\varepsilon=0}. \end{aligned} \tag{23}$$

$\delta E_{\rho_0}[\delta\rho; \mathbf{r}]$ is called the *variation* of the energy with respect to the perturbation, $\delta\rho(\mathbf{r})$, of the electron density $\rho_0(\mathbf{r})$. The functional derivative exists when $\delta E_{\rho_0}[\delta\rho; \mathbf{r}]$ is a linear functional of $\delta\rho(\mathbf{r})$ [68].

3.2 The variational principle and the chemical potential

Recall that at a minimum, $\mathbf{x}_{\min}$, the value of a differentiable function, $f(\mathbf{x})$ is stationary with respect to small variations in $\mathbf{x}_{\min}$; equivalently, $\nabla_{\mathbf{x}} f(\mathbf{x}_{\min}) = 0$. The second Hohenberg–Kohn theorem implies an analogue of this result [62]: the ground state energy of system with N-electrons in the external potential $v(\mathbf{r})$ is stationary with respect to small number-conserving variations about the ground state density. Stated mathematically:

$$\left(\frac{\partial E_v[\rho_N(\mathbf{r}) + \varepsilon\cdot g(\mathbf{r})]}{\partial\varepsilon}\right)_{\varepsilon=0} = 0, \tag{24}$$

where $\rho_N(\mathbf{r})$ is the ground state density for the N-electron system with external potential $v(\mathbf{r})$ and $g(\mathbf{r})$ is any

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[4] Strictly speaking the functional derivative must be in the dual space to the space of density variations under consideration. This mathematical nuance will not be important here, however.

"conventional" function [69] that is normalized to zero,

$$\int g(\mathbf{r})d\mathbf{r} = 0. \tag{25}$$

The restriction to variations satisfying (25) is necessary because the variational principle for the energy only applies to electron densities with the same number of electrons. Using (20) and denoting the ground state electron density of the $N+\varepsilon$ electron system as $\rho_{N+\varepsilon}(\mathbf{r})$, gives

$$\begin{aligned}
&\frac{\delta E_v[\rho_N]}{\delta\rho(\mathbf{r}_0)} \\
&\equiv \underbrace{\lim}_{\varepsilon\to 0} \frac{E_v[\rho_N(\mathbf{r})+\varepsilon\delta(\mathbf{r}-\mathbf{r}_0)] - E_v[\rho_N(\mathbf{r})]}{\varepsilon} \\
&= \underbrace{\lim}_{\varepsilon\to 0} \frac{E_v[\rho_N(\mathbf{r})+\varepsilon\delta(\mathbf{r}-\mathbf{r}_0)] - E_v[\rho_{N+\varepsilon}(\mathbf{r})]}{\varepsilon} \\
&\quad + \underbrace{\lim}_{\varepsilon\to 0} \frac{E_v[\rho_{N+\varepsilon}(\mathbf{r})] - E_v[\rho_N(\mathbf{r})]}{\varepsilon} \\
&= \underbrace{\lim}_{\varepsilon\to 0} \frac{E_v\left[\rho_{N+\varepsilon}(\mathbf{r})+\varepsilon\left\{\delta(\mathbf{r}-\mathbf{r}_0) - \frac{\rho_{N+\varepsilon}(\mathbf{r})-\rho_N(\mathbf{r})}{\varepsilon}\right\}\right] - E_v[\rho_{N+\varepsilon}(\mathbf{r})]}{\varepsilon} \\
&\quad + \underbrace{\lim}_{\varepsilon\to 0} \frac{E[v;N+\varepsilon] - E[v;N]}{\varepsilon} \\
&= \left(\frac{\partial E_v\left[\rho_{N+\varepsilon}(\mathbf{r})+\varepsilon\left\{\delta(\mathbf{r}-\mathbf{r}_0) - \frac{\rho_{N+\varepsilon}(\mathbf{r})-\rho_N(\mathbf{r})}{\varepsilon}\right\}\right]}{\partial\varepsilon}\right)_{\varepsilon=0} \\
&\quad + \left(\frac{\partial E[v;N]}{\partial N}\right)_{v(\mathbf{r})} \\
&= \left(\frac{\partial E[v;N]}{\partial N}\right)_{v(\mathbf{r})}.
\end{aligned} \tag{26}$$

Equations (24) and (25) are used in the last step: the term in braces reduces to a number conserving variation of the density. Using the definition of the electronic chemical potential [cf. Eq. (1)] [1],

$$\frac{\delta E_v[\rho_N]}{\delta\rho(\mathbf{r})} = \mu[v;N]. \tag{27}$$

Equation (27) states the second Hohenberg–Kohn theorem in the form of a functional differential equation for the ground state density. This equation is directly analogous to the functional differential expression of the variational principle for the wavefunction

$$\frac{\delta\frac{\left\langle\Psi\left|\hat{H}[v;N]\right|\Psi\right\rangle}{\langle\Psi|\Psi\rangle}}{\delta\Psi} \equiv \frac{\delta E_{v;N}[\Psi]}{\delta\Psi} = 0, \tag{28}$$

Unlike (28), which holds also for excited state wavefunctions, (27) generally holds only for the ground state [69,70].

There is a subtle point in the derivation of Eq. (26). The "number conserving variation" that is set to zero depends on ε. To make this step more rigorous, expand $\rho_{N+\varepsilon}(\mathbf{r})-\rho_N(\mathbf{r})$ in a Taylor series,

$$\rho_{N+\varepsilon}(\mathbf{r}) - \rho_N(\mathbf{r}) = \sum_{n=1}^{\infty}\frac{\varepsilon^n}{n!}\left(\frac{\partial^n\rho_N(\mathbf{r})}{\partial N^n}\right)_{v(\mathbf{r})}. \tag{29}$$

and then

$$\begin{aligned}
&\left(\frac{\partial E_v\left[\rho_{N+\varepsilon}(\mathbf{r})+\varepsilon\left\{\delta(\mathbf{r}-\mathbf{r}_0) - \frac{\rho_{N+\varepsilon}(\mathbf{r})-\rho_N(\mathbf{r})}{\varepsilon}\right\}\right]}{\partial\varepsilon}\right)_{\varepsilon=0} \\
&= \left(\frac{\partial E_v\left[\rho_{N+\varepsilon}(\mathbf{r})+\varepsilon\left\{\delta(\mathbf{r}-\mathbf{r}_0) - \left(\frac{\partial\rho_N(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})}\right\}\right]}{\partial\varepsilon}\right)_{\varepsilon=0} \\
&\quad + \left(\frac{\partial E_v\left[\sum_{n=2}^{\infty}\varepsilon^n\left(\frac{\partial^n\rho_N(\mathbf{r})}{\partial N^n}\right)_{v(\mathbf{r})}\right]}{\partial\varepsilon}\right)_{\varepsilon=0} \\
&= 0
\end{aligned} \tag{30}$$

The first term is zero because it is the change in energy due to a number-conserving variation of the electron density. The second term is zero because the derivative of a function of the form $f(\varepsilon) = a_2\varepsilon^2 + a_3\varepsilon^3 + \cdots$ is zero at $\varepsilon = 0$.

3.3 The constancy of the chemical potential

The chemical potential equalization principle follows directly from (27). Define the local chemical potential by

$$\mu(\mathbf{r}) \equiv \frac{\delta E_v[\rho]}{\delta\rho(\mathbf{r})}. \tag{31}$$

If $\rho_v(\mathbf{r})$ is a ground state density for the external potential under scrutiny, then $\mu(\mathbf{r}) = \mu$—the chemical potential is equalized throughout the molecule. However, if $\rho(\mathbf{r})$ is not a ground state density, then we can find two points, $\mathbf{r}_1$ and $\mathbf{r}_2$, such that $\mu(\mathbf{r}_1) < \mu(\mathbf{r}_2)$. Consider these two points to be separate systems with

$$N_1 = \rho(\mathbf{r}_1)d\mathbf{r} \tag{32}$$

and

$$N_2 = \rho(\mathbf{r}_2)d\mathbf{r} \tag{33}$$

electrons. The system with

$$\begin{aligned}
N_1 + dN &= (\rho(\mathbf{r}_1) + \delta\rho(\mathbf{r}))d\mathbf{r} \\
N_2 - dN &= (\rho(\mathbf{r}_2) - \delta\rho(\mathbf{r}))d\mathbf{r}
\end{aligned} \tag{34}$$

has lower energy than the original system; hence, an electronic system is not stable with respect to perturbations in the electron density unless the chemical potential is constant throughout the system, $\mu(\mathbf{r}) = \mu$. This implies that the chemical potential is constant for any system in its electronic ground state.

The preceding derivation presumes that the energy is a differentiable function of the number of electrons; this analysis will be valid for a molecule in solution or for a molecule described by a grand canonical ensemble with a nonzero "effective temperature." In those cases the chemical potential of the molecule is a single, well-defined constant.

When one considers a molecule in isolation, the zero-temperature grand canonical ensemble is most appropriate and the energy is given by the piecewise linear form in Eq. (4). The energy is no longer differentiable when the number of electrons is an integer. The one-sided derivatives still exist, however, and so distinct chemical potentials for electron addition, μ^+, and electron removal, μ^-, can be defined:

$$\begin{aligned}\mu^+[v;N] &= \left(\frac{\partial E[v;N]}{\partial N}\right)^+_{v(\mathbf{r})} \\ &= E[v;N+1]-E[v;N] = -A \qquad (35)\\ \mu^-[v;N] &= \left(\frac{\partial E[v;N]}{\partial N}\right)^-_{v(\mathbf{r})} \\ &= E[v;N]-E[v;N-1] = -I\end{aligned}$$

These expressions will be very important in the subsequent analysis. μ^+ is the appropriate chemical potential for describing perturbations of the electron density that increase the number of electrons; μ^- is the appropriate chemical potential for describing perturbations that decrease the number of electrons. For an isolated molecule that is not dissociated (all of the atoms are within a finite distance of each other), the chemical potential from above, μ^+, and the chemical potential from below, μ^-, are constants, and do not depend on the position in the molecule where the electron density is increased (μ^+) or decreased (μ^-). Symbolically,

$$\begin{aligned}\mu^+[v;N] &= \text{constant} = \left(\frac{\delta E_v[\rho]}{\delta\rho(\mathbf{r})}\right)^+ \\ &= \left(\frac{\partial E_v[\rho(\mathbf{r})+\varepsilon\delta(\mathbf{r}-\mathbf{r}_0)]}{\partial\varepsilon}\right)^+_{\varepsilon=0} \qquad (36)\\ \mu^-[v;N] &= \text{constant} = \left(\frac{\delta E_v[\rho]}{\delta\rho(\mathbf{r})}\right)^- \\ &= \left(\frac{\partial E_v[\rho(\mathbf{r})+\varepsilon\delta(\mathbf{r}-\mathbf{r}_0)]}{\partial\varepsilon}\right)^-_{\varepsilon=0}\end{aligned}$$

The preceding arguments, however, do not extend to the case where a molecule has dissociated into two subsystems that are infinitely far apart. This special case—where μ^+ and μ^- are not necessarily unique or position-independent—is studied in the next section.

4 Non-locality and the chemical potential

4.1 The chemical potential paradox

For molecules, the chemical potential equalization principle is rigorously valid and, as seen in the preceding section, can be understood without any unusual conceptual calisthenics. When a molecule dissociates, however, a paradox arises. Consider again the system considered in the introduction: when a Cesium Fluoride ion dissociates, it dissociates into the neutral atoms (Cs and F). The chemical potential equalization principle indicates that if you measure the chemical potential for electron addition, μ^+, this is equal to the minus the electron affinity of the Fluorine atom,

$$\mu^+_{\mathrm{Cs\cdots F}} = \min\left(\mu^+_{\mathrm{F}}, \mu^+_{\mathrm{Cs}}\right) = \mu^+_{\mathrm{F}} = -A_{\mathrm{F}}. \qquad (37)$$

This is paradoxical; it would suggest that the energy that is released when an electron is added to the Cesium atom is given by the electron affinity of the Fluorine atom, even though that atom is infinitely far away. This contradicts our understanding of physics: the properties of the Cesium atom should not be affected by the properties of another atom that is infinitely far away.

There is, in fact, no "nonlocality paradox" for the chemical potential. For a dissociated molecule, the functional derivative of the energy with respect to the electron density does not exist. This means the chemical potential is not uniquely defined[5]. Instead, there are different "apparent chemical potentials" that depend on the way that the system is perturbed. If the electron density is increased in the vicinity of the Cesium atom, then the "apparent" chemical potential is $-A_{\mathrm{Cs}}$, in accord with the locality of the perturbation. If the electron density is increased in the vicinity of the Fluorine atom, then the "apparent" chemical potential is $-A_{\mathrm{F}}$, also in accord with expectations. There is no chemical potential nonlocality paradox because: (a) The chemical potential does not exist in this case. (b) Instead, there is an "apparent" chemical potential depends on where one perturbs the system. (c) The response to a local perturbation of an atom's electron density is not affected by another atom infinitely far away.

The preceding facts are based on the size consistency of the molecule's properties. That is, as the molecule dissociates, the properties of the molecule become the sum of the individual subsystem properties. This is true, in particular,

---

[5] More precisely, for heteroatomic dissociated molecules, Eq. (31) for the "local" chemical potential does not give a constant, and so it is impossible to describe the entire system with a single value of the chemical potential for the entire system. In this sense, the chemical potential of dissociated molecules does not exist.

for the energy and the electron density:

$$\underbrace{\lim}_{R\to\infty} E_{\mathrm{CsF}} = E_{\mathrm{Cs}} + E_{\mathrm{F}} \tag{38}$$

$$\underbrace{\lim}_{R\to\infty} \rho_{\mathrm{CsF}}(\mathbf{r}) = \rho_{\mathrm{Cs}}(\mathbf{r}) + \rho_{\mathrm{F}}(\mathbf{r}) \tag{39}$$

The Hohenberg–Kohn functional is also size consistent since

$$\begin{aligned}
&\underbrace{\lim}_{R\to\infty} F[\rho_{\mathrm{CsF}}] \\
&= \underbrace{\lim}_{R\to\infty} \left(E_{\mathrm{CsF}} - \int \rho_{\mathrm{CsF}}(\mathbf{r}) \ \times (v_{\mathrm{Cs}}(\mathbf{r}) + v_{\mathrm{F}}(\mathbf{r}))\, d\mathbf{r} \right) \\
&= E_{\mathrm{Cs}} - \int \rho_{\mathrm{Cs}}(\mathbf{r}) v_{\mathrm{Cs}}(\mathbf{r}) d\mathbf{r} + E_{\mathrm{F}} - \int \rho_{\mathrm{F}}(\mathbf{r}) v_{\mathrm{F}}(\mathbf{r}) d\mathbf{r} \\
&= F[\rho_{\mathrm{Cs}}] + F[\rho_F]
\end{aligned} \tag{40}$$

This is a special case of the general result: $F[\rho_{\mathrm{A}} + \rho_{\mathrm{B}}] = F[\rho_{\mathrm{A}}] + F[\rho_{\mathrm{B}}]$ is true whenever the subsystem densities are infinitely far apart [39]. This argument in Eq. (40) is valid when the electron density of the supermolecule, $\rho_{\mathrm{A}}(\mathbf{r}) + \rho_{\mathrm{B}}(\mathbf{r})$, is v-representable. When this is not the case, the same result can be derived using Lieb's Legendre transform functional [66]. (However, if $\rho_{\mathrm{A}}(\mathbf{r}) + \rho_{\mathrm{B}}(\mathbf{r})$ is not v-representable, then this result does *not* hold for the Levy constrained search functional [63]! The undesirability of this "spooky action at a distance" suggests that the size consistency of $F[\rho]$ should be imposed as an axiom, which every reasonable definition of $F[\rho]$ must satisfy [65].)

The chemical potential can be evaluated by measuring the response of the electronic energy to a small number-increasing perturbation of the electron density that is localized near the point $\mathbf{r}_0$, $\delta_{\mathbf{r}_0}\rho(\mathbf{r})$. If the perturbation is near the Cesium atom, then

$$\begin{aligned}
&E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}\left[\rho_{\mathrm{CsF}}(\mathbf{r}) + \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})\right] - E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}[\rho_{\mathrm{CsF}}(\mathbf{r})] \\
&\quad = F\left[\rho_{\mathrm{CsF}} + \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho\right] \\
&\qquad + \int \left(\rho_{\mathrm{CsF}}(\mathbf{r}) + \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})\right)(v_{\mathrm{Cs}}(\mathbf{r}) + v_{\mathrm{F}}(\mathbf{r}))d\mathbf{r} \\
&\qquad - F[\rho_{\mathrm{CsF}}] - \int \rho_{\mathrm{CsF}}(\mathbf{r})(v_{\mathrm{Cs}}(\mathbf{r}) + v_{\mathrm{F}}(\mathbf{r}))d\mathbf{r}
\end{aligned} \tag{41}$$

The size consistency of $F[\rho]$ and the locality of the external potentials for the Cesium and Fluorine atoms then implies that

$$\begin{aligned}
&E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}\left[\rho_{\mathrm{CsF}}(\mathbf{r}) + \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})\right] - E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}[\rho_{\mathrm{CsF}}(\mathbf{r})] \\
&\quad = F\left[\rho_{\mathrm{Cs}} + \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho\right] + F[\rho_{\mathrm{F}}] \\
&\qquad + \int \left(\rho_{\mathrm{Cs}}(\mathbf{r}) + \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})\right) v_{\mathrm{Cs}}(\mathbf{r}) d\mathbf{r} + \int \rho_{\mathrm{F}}(\mathbf{r}) v_{\mathrm{F}}(\mathbf{r}) d\mathbf{r} \\
&\qquad - F[\rho_{\mathrm{Cs}}] - F[\rho_{\mathrm{F}}] - \int \rho_{\mathrm{Cs}}(\mathbf{r}) v_{\mathrm{Cs}}(\mathbf{r}) d\mathbf{r} - \int \rho_{\mathrm{F}}(\mathbf{r}) v_{\mathrm{F}}(\mathbf{r}) d\mathbf{r} \\
&\quad = E_{v_{\mathrm{Cs}}}\left[\rho_{\mathrm{Cs}} + \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho\right] - E_{v_{\mathrm{Cs}}}[\rho_{\mathrm{Cs}}]
\end{aligned} \tag{42}$$

$$\begin{aligned}
&= \int \left(\mu^{+}_{\mathrm{Cs}}\right) \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r}) d\mathbf{r} \\
&= \int (-A_{\mathrm{Cs}}) \delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r}) d\mathbf{r}
\end{aligned}$$

Similarly, if the perturbation is centered on the Fluorine atom,

$$\begin{aligned}
&E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}\left[\rho_{\mathrm{CsF}}(\mathbf{r}) + \delta_{\mathbf{r}_{\mathrm{F}}}\rho(\mathbf{r})\right] - E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}[\rho_{\mathrm{CsF}}(\mathbf{r})] \\
&\quad = E_{v_{\mathrm{F}}}\left[\rho_{\mathrm{F}} + \delta_{\mathbf{r}_{\mathrm{F}}}\rho\right] - E_{v_{\mathrm{F}}}[\rho_{\mathrm{F}}] \\
&\quad = \int \left(\mu^{+}_{\mathrm{F}}\right) \delta_{\mathbf{r}_{\mathrm{F}}}\rho(\mathbf{r}) d\mathbf{r} \\
&\quad = \int (-A_{\mathrm{F}}) \delta_{\mathbf{r}_{\mathrm{F}}}\rho(\mathbf{r}) d\mathbf{r}
\end{aligned} \tag{43}$$

Since the electron affinity of Fluorine is greater than the electron affinity of Cesium, perturbing the system on the Fluorine atom elicits a larger response than perturbing the system on the Cesium atom. The change in energy is *not* a linear functional of the perturbation. Instead, the change in energy depends on the specific nature of the perturbation and, in particular, whether the perturbation is "on the Fluorine atom" or "on the Cesium atom." Referring back to the discussion in Sect. 3.1., the *variation* of the energy can be evaluated, but the functional derivative does not exist. Since the functional derivative of the energy with respect to the electron density, evaluated at the ground state density, is identified as the chemical potential of the system, the chemical potential also does not exist. More precisely, the chemical potential of the system is not unique because the "apparent value" of the chemical potential depends on the nature of the perturbation.

Figure 1 provides a pictorial representation of the phenomenon. There are two apparent chemical potentials for

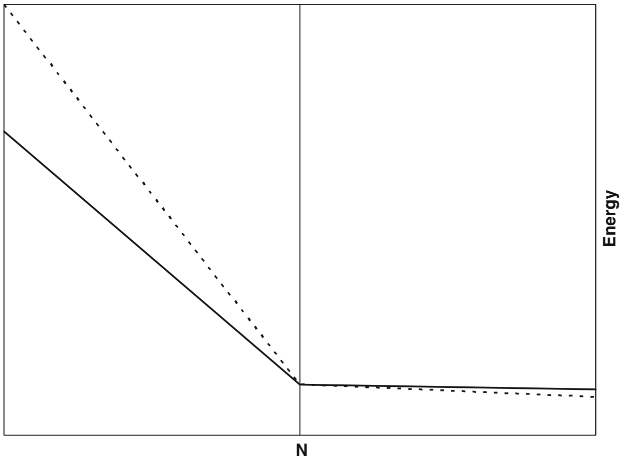

Fig. 1 The energy is plotted as a function of the number of electrons for dissociated Cesium Fluoride; the slope of the *lines* indicates the chemical potentials. There are different chemical potentials corresponding to electron addition/removal near the Cesium center (*solid lines*) or the Fluorine center (*dashed lines*).

electron attachment [Eqs. (42), and (43)] and, similarly, two apparent chemical potentials for electron removal:

$$
\begin{aligned}
&E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}\left[\rho_{\mathrm{CsF}}(\mathbf{r})-\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})\right]-E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}[\rho_{\mathrm{CsF}}(\mathbf{r})]\\
&\quad=E_{v_{\mathrm{Cs}}}\left[\rho_{\mathrm{Cs}}-\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho\right]-E_{v_{\mathrm{Cs}}}[\rho_{\mathrm{Cs}}]\\
&\quad=\int\left(\mu_{\mathrm{Cs}}^{-}\right)\left(-\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})\right)d\mathbf{r} \qquad (44)\\
&\quad=\int\left(-I_{\mathrm{Cs}}\right)\left(-\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})\right)d\mathbf{r}
\end{aligned}
$$

$$
\begin{aligned}
&E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}\left[\rho_{\mathrm{CsF}}(\mathbf{r})-\delta_{\mathbf{r}_{\mathrm{F}}}\rho(\mathbf{r})\right]-E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}[\rho_{\mathrm{CsF}}(\mathbf{r})]\\
&\quad=E_{v_{\mathrm{F}}}\left[\rho_{\mathrm{F}}-\delta_{\mathbf{r}_{\mathrm{F}}}\rho\right]-E_{v_{\mathrm{F}}}[\rho_{\mathrm{F}}]\\
&\quad=\int\left(\mu_{\mathrm{F}}^{-}\right)\left(-\delta_{\mathbf{r}_{\mathrm{F}}}\rho(\mathbf{r})\right)d\mathbf{r} \qquad (45)\\
&\quad=\int\left(-I_{\mathrm{F}}\right)\left(-\delta_{\mathbf{r}_{\mathrm{F}}}\rho(\mathbf{r})\right)d\mathbf{r}
\end{aligned}
$$

There is no "chemical potential nonlocality paradox" because the "apparent chemical potentials" are determined by the location of the perturbation. Thus the measured response of a system to a perturbation in its electron density is independent of the possible presence of other systems, infinitely far away. The locality of the energy's response to perturbations means that it is impossible to define a single chemical potential of the "supermolecule." That is, since the functional derivative of the "supermolecule" with respect to the electron density is not defined, it is impossible to unambiguously determine the chemical potential for the entire supermolecule[6].

4.2 Relationship to excited-state density-functional theory

For an ordinary molecule, the energy functional, $E_v[\rho]$, is convex [65,66,71,72]. Because of this, it has only one stationary value; this single stationary value gives rise to a single chemical potential. For a dissociated molecule, there is no single stationary value for the chemical potential. This is because the energy functional must be capable of describing not only the ground state, but also charge-transfer excited states. For example, because the energy functional can describe both the cations and the anions of Cesium and Fluorine, it should be able to describe the following charge-transfer excited states of the Cesium Fluoride molecule:

$$
\begin{aligned}
&\mathrm{Cs}\cdots\mathrm{F}\\
&\mathrm{Cs}^{+}\cdots\mathrm{F}^{-} \qquad (46)\\
&\mathrm{Cs}^{-}\cdots\mathrm{F}^{+}
\end{aligned}
$$

Levy and Perdew showed that if an energy functional can describe an excited state, then the energy is not stationary with respect to density perturbations "in the direction of" that excited state [69]. Let $\delta_{\mathbf{r}_0}\rho(\mathbf{r})$ and $\delta_{\mathbf{r}_0}\tilde{\rho}(\mathbf{r})$ denote two different perturbations of the electron density around the point $\mathbf{r}_0$, both of which increase the number of electrons by the same amount. The energy is stationary with respect to number-preserving perturbations of the electron density as long as the perturbations are localized on one atom. E.g.,

$$
\begin{aligned}
&E_{v_{\mathrm{Cs}}}+v_{\mathrm{F}}\left[\rho_{\mathrm{CsF}}(\mathbf{r})-\delta_{\mathbf{r}_F}\rho(\mathbf{r})+\delta_{\mathbf{r}_{\mathrm{F}}}\tilde{\rho}(\mathbf{r})\right]\\
&\quad-E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}[\rho_{\mathrm{CsF}}(\mathbf{r})]\\
&\quad=E_{v_{\mathrm{F}}}\left[\rho_{\mathrm{F}}-\delta_{\mathbf{r}_F}\rho+\delta_{\mathbf{r}_{\mathrm{F}}}\tilde{\rho}\right]-E_{v_{\mathrm{F}}}[\rho_{\mathrm{F}}] \qquad (47)\\
&\quad=(-\mu_{\mathrm{F}})\int\left(-\delta_{\mathbf{r}_{\mathrm{F}}}\rho(\mathbf{r})+\delta_{\mathbf{r}_{\mathrm{F}}}\tilde{\rho}(\mathbf{r})\right)d\mathbf{r}\\
&\quad=0
\end{aligned}
$$

However, if the perturbation of the electron density represents charge transfer, then the energy is not stationary; instead, the energy increases in proportion to the magnitude of the electron transfer.

$$
\begin{aligned}
&E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}\left[\rho_{\mathrm{CsF}}(\mathbf{r})+\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})-\delta_{\mathbf{r}_F}\tilde{\rho}(\mathbf{r})\right]\\
&\quad-E_{v_{\mathrm{Cs}}+v_{\mathrm{F}}}[\rho_{\mathrm{CsF}}(\mathbf{r})]\\
&\quad=E_{v_{\mathrm{Cs}}}\left[\rho_{\mathrm{Cs}}+\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho\right]-E_{v_{\mathrm{Cs}}}[\rho_{\mathrm{Cs}}]\\
&\qquad+E_{v_{\mathrm{F}}}\left[\rho_{\mathrm{F}}-\delta_{\mathbf{r}_F}\tilde{\rho}\right]-E_{v_{\mathrm{F}}}[\rho_{\mathrm{F}}] \qquad (48)\\
&\quad=\int\mu_{\mathrm{Cs}}^{+}\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})d\mathbf{r}-\int\mu_{\mathrm{F}}^{-}\delta_{\mathbf{r}_{\mathrm{F}}}\tilde{\rho}(\mathbf{r})d\mathbf{r}\\
&\quad=(I_{\mathrm{F}}-A_{\mathrm{Cs}})\int\delta_{\mathbf{r}_{\mathrm{Cs}}}\rho(\mathbf{r})d\mathbf{r}
\end{aligned}
$$

The ground state energy of a dissociated molecule is stationary with respect to "localized" number-conserving variations of the electron density but it is not always stationary with respect to "delocalized" number-conserving variations, because those variations correspond to charge-transfer excitations, and are thus "unconventional perturbations" of the ground state [69].

Another way to understand this phenomenon is to note that all of the charge-transfer "excited states" in Eq. (46) are in fact ground states for a suitably choice of external potential where, for example, potential in the vicinity of the Cesium atom is shifted upwards by a constant, $I_{\mathrm{Cs}}-A_{\mathrm{F}}$. (In the new external potential, electron transfer from Cs to F can spontaneously occur.) Because charge-transfer excited state densities of the normal atomic potentials $(v_{\mathrm{Cs}}(\mathbf{r})+v_{\mathrm{F}}(\mathbf{r}))$ are ground-state densities for the shifted atomic potentials, this is a special case where a "ground-state density functional" will give the correct result for certain special excited states.

The fact that the functional derivative, $\frac{\delta E_v[\rho]}{\delta\rho(\mathbf{r})}$, and thus the chemical potential, does not exist is a direct consequence of the fact that this energy functional is stationary not only for the ground state, but also for certain excited states. If one designs a functional that is stationary for some, or even all,

---

[6] From this perspective, there is cannot be a "chemical potential equalization paradox" for a dissociated molecule because, mathematically speaking, the chemical potential of the dissociated molecule does not exist!

excited states, then one has multiple chemical potentials, $\mu_{kl}^{\pm}$,

$$\mu_{kl}^{\pm} = \begin{cases} E_l^{N+1} - E_k^N \\ E_k^N - E_l^{N-1} \end{cases} \tag{49}$$

and there are different "apparent chemical potentials" for different perturbations of the electron density[2]. For dissociated systems, the size-consistency of the energy functional forces it to be able to model the charge-transfer excited states and the different "apparent chemical potentials" associated with different perturbations of the electron density reflect this fact.

The fact long-range electron-transfer is readily modeled by time-independent functionals in density-functional theory suggests that perhaps time-independent approaches to excited-state DFT [73–76] should be preferred to time-dependent approaches for charge-transfer excited states. Some preliminary indications of how this might work is already contained in the work of Wu and Van Voorhis [77, 78], where a "constraint potential" is used to ensure that the "apparent chemical potential" of the electron donor and the electron acceptor are different. The present work reveals that the difference in the "apparent chemical potential" of the fragments arises very naturally when the electron donor and the electron acceptor are infinitely far apart, and so extending this behavior to finite separations is a pragmatic, but theoretically justifiable, approximation.

5 Discussion

It should be stressed that there is no chemical potential paradox for systems at large, but finite, separations. In this case the chemical potential is well defined and equalized throughout the molecule. As an extreme example, consider the Cesium Fluoride molecule again, but allow the Cesium and the Fluorine nuclei to be R meters apart. As long as the atoms are well separated, the chemical potential for electron removal will be well-approximated using the ionization potential of Cesium,

$$\mu_{\rm CsF}^{-} \approx \mu_{\rm Cs}^{-} = -I_{\rm Cs}. \tag{50}$$

This may seem counterintuitive. Suppose one aimed a laser at the Fluorine atom and ionized it; this produces an excited state of the molecule, namely $\mathrm{Cs} \cdots\cdots \mathrm{F}^{+}$. (However, because the atoms are a finite distance apart, $E_v[\rho]$ is not stationary for this electron density.) After some time, an electron would tunnel from the Cesium atom to the Fluorine cation and radiation with energy proportional to the ionization potential difference, $I_{\rm F} - I_{\rm Cs}$, would be emitted. If the systems are very far apart, then this relaxation process is very slow. However, in a *time-independent* theory, one can only sees the long-time limit of this process. Thus one observes the chemical potential that is associated with the Cesium atom even if the perturbation in question is localized on the Fluorine atom that is a large (but finite) distance away:

$$\begin{aligned} &E_{v_{\rm Cs}+v_{\rm F};R<\infty}\left[\rho_{\rm CsF}(\mathbf{r}) - \delta_{\mathbf{r}_{\rm F}}\rho(\mathbf{r})\right] - E_{v_{\rm Cs}+v_{\rm F};R<\infty}[\rho_{\rm CsF}(\mathbf{r})] \\ &\quad \approx \int (-I_{\rm Cs})\left(-\delta_{\mathbf{r}_{\rm F}}\rho(\mathbf{r})\right)d\mathbf{r} \end{aligned} \tag{51}$$

As the internuclear distance increases further, this tunneling process becomes slower and slower. In the limit of infinite separation, the tunneling rate is zero and the state $\mathrm{Cs} \cdots\cdots \mathrm{F}^{+}$ emerges as a stationary state of the ionized molecule.

There is not a chemical potential paradox when the subsystems are infinitely far apart because *there is no chemical potential in this case* (unless the subsystems are chemically identical). That is, the chemical potential of infinitely separated subsystems is ill-defined: different perturbations of the electron density are associated with different "apparent chemical potentials." The "apparent chemical potential" for electron removal from the Fluorine atom is $-I_{\rm F}$; the "apparent chemical potential" for electron removal from the Cesium atom is $-I_{\rm Cs}$. There is no "nonlocality paradox" because the response of a system to a change in electron density does not depend on other systems that are infinitely far away.

Though this paper focuses on the "locality" of the chemical potential, some of the results in Sect. 2 may be of independent interest. In particular, the heuristic model for the energy versus the number of electrons helps explain the utility of the nonzero temperature grand canonical ensemble in density functional reactivity theory. The approximate model proposed here [cf. Eq. (10)] with an effective temperature that depends on the extent of molecular polarization has an advantage over many competing theories since it reduces to the correct "zero-temperature" limit in the appropriate cases: isolated molecules, noninteracting solvents, and infinitely separated subsystems.

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