

The dependence on and continuity of the energy and other molecular properties with respect to the number of electrons

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It was recently shown that the size consistency of the energy implies that, for any system with a rational number of electrons, the energy is given by the weighted average of the two systems with the nearest integer numbers of electrons. Specifically, $E[N+P/Q] = (1-P/Q)E[N] + (P/Q)E[N+1]$. This paper extends that analysis, showing that the same result holds for irrational numbers of electrons. This proves that the energy is a continuous function of the number of electrons, and justifies differentiation with respect to electron number, providing a rigorous justification for the density-functional theoretic approaches to chemical concepts like the electronegativity and the Fukui function. Similar results hold for properties other than the energy. Specific emphasis is placed on molecular response properties associated with the density-functional theory of chemical reactivity.

KEY WORDS: zero-temperature grand canonical ensemble, derivative discontinuity, conceptual density functional theory, chemical reactivity

1. Introduction

As density-functional theory (DFT) [1–4] has gained acceptance as a computational chemistry method, many of the outstanding theoretical problems underlying the theory have been overlooked as researchers aim instead to participate in the glamorous task of functional development. When functional development stagnates, the way forward is inevitably a return to the theoretical underpinnings of DFT and, in particular, theoretical properties of exact density functionals that are not fulfilled by present approximations. One such property is the discontinuity in functional derivatives with respect to the electron density at integer numbers of electrons [5, 6], and another is the “linear mixing law” that relates how observable properties of systems change as the number of electrons changes [7]. Present functionals mimic neither behavior which, among other things, leads to unreliable calculations of band gaps and functionals that

fail badly for highly charged molecular species. Characterizing the behavior of density functionals as the number of electrons changes, then, is an important prerequisite for improving existing approximations.

Distressingly, some of the most elementary questions about how properties depend on electron number still remain answered. In this paper, we address one of the most fundamental possible questions: is the energy a continuous function of the number of electrons? That is, does a slight displacement of a system's electron density toward either its cation or anion always give a similarly slight change in energy? One might presume that the energy is "obviously" continuous in this way and, indeed, the entire edifice of the DFT of chemical reactivity [8–11]—wherein differentiation with respect to the number of electrons is used to define the electronegativity [12, 13], hardness [14–16], Fukui function [17–21], and other properties—is based on this *assumption*. As the forthcoming analysis shows, the reason that the energy is continuous is by no means trivial.

The analysis in this paper is based on the treatment of Ref. [7], which is summarized and extended in section 2. In section 3, the implications of this analysis are discussed, with particular emphasis on the response properties used in the DFT of chemical reactivity.

2. Mathematical results

2.1. Review

Reference [7] presents an especially simple approach to the fractional electron number problem. Unlike the common approaches based on the zero temperature grand canonical ensemble [5, 6, 22], this approach does not introduce a fictitious temperature and take the zero temperature limit. The basic idea is to construct the zero temperature grand canonical ensemble one replica at a time. Consider Q replicas of an N -electron molecule, with the replicas spaced far enough apart so that the interaction between them can be neglected. If we add P extra electrons to the supermolecule ($P < Q$), the ground-state energy of the supermolecule will be P times the energy of the $(N + 1)$ -electron molecule, plus $Q - P$ times the energy of the N -electron molecule:

$$E_{\text{total}} = P E_{\text{replica}}^{(N+1)} + (Q - P) E_{\text{replica}}^{(N)}, \quad (1)$$

where $E_{\text{replica}}^{(N)}$ is the N -electron ground-state energy of a single replica. However, all of the replicas are identical, so they can be chosen to have the same energy,

$$E_1 = E_2 = \dots = E_{Q-1} = E_Q. \quad (2)$$

Because the replicas do not interact, the sum of the energy of the replicas must be equal to the total energy and so, from equations (1) and (2), the energy of a replica is

$$E_q = \frac{P}{Q} E_{\text{replica}}^{(N+1)} + \left(1 - \frac{P}{Q}\right) E_{\text{replica}}^{(N)} \tag{3}$$

In equation (3) and what follows, lower-case letters (p, q, r, \dots) are used to indicate the properties of a specific replica.

Equation (2) can be generalized to properties other than the energy: because all the replicas are identical, they can be chosen to have identical properties.

$$A_1 = A_2 = \dots = A_Q. \tag{4}$$

If the property, A , is size consistent, then the total value of A is the sum of its values for the noninteracting replicas, leading to an expression like equation (3)

$$A_q = \frac{P}{Q} A_{\text{replica}}^{(N+1)} + \left(1 - \frac{P}{Q}\right) A_{\text{replica}}^{(N)}, \tag{5}$$

where $A_{\text{replica}}^{(N)} = \langle \Psi_{\text{replica}}^{(N)} | \hat{A} | \Psi_{\text{replica}}^{(N)} \rangle$ is the value of the property in the N -electron ground state of a replica. Equation (5) holds, in particular, for the number of electrons in a replica. Thus, all the replicas can be chosen to have equal numbers of electrons, and equation (3) can be used to define the value of the energy for any rational number of electrons:

$$E_{\text{replica}}^{\left(N + \frac{P}{Q}\right)} = \frac{P}{Q} E_{\text{replica}}^{(N+1)} + \left(1 - \frac{P}{Q}\right) E_{\text{replica}}^{(N)}, \quad 0 \leq P \leq Q. \tag{6}$$

Equation (5) can be used to define the values of other size-consistent properties,

$$A_{\text{replica}}^{\left(N + \frac{P}{Q}\right)} = \frac{P}{Q} A_{\text{replica}}^{(N+1)} + \left(1 - \frac{P}{Q}\right) A_{\text{replica}}^{(N)}, \quad 0 \leq P \leq Q. \tag{7}$$

This argument is the essence of Ref. [7]. (The extension to operators other than the energy is new, but it is a trivial corollary of that analysis.) This argument is only valid for rational numbers of electrons, since it requires that P and Q be integers. One goal of this paper is to extend this analysis to irrational numbers, so that the properties of a system with an irrational number of electrons can be inferred. Doing this requires filling in the mathematical details that underlie the preceding discussion.

2.2. *Mathematical details: fractional electron number*

Suppose that we are given a system where the electrons are bound by an external potential $v(\mathbf{r})$. This external potential is assumed to be local, so that,

$$\underbrace{\lim}_{r \rightarrow \infty} v(r, \theta, \phi) = 0. \tag{8}$$

With such a potential, systems that are infinitely far apart do not interact. For atoms and molecules the external potential is just the electron–nuclear potential, which has the form

$$v(\mathbf{r}) = \sum_{\alpha=1}^{N_{\text{atoms}}} \frac{-Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}. \quad (9)$$

Equation (8) is not always true; it is not true in the noninteracting limit of a Kohn–Sham DFT calculation, for example, though there is no special problem in that case because the identity is violated only on sets of zero measure [23–25].

Now, let us replicate our system, putting Q copies of our system at spatially distinct points, $\mathbf{X}_1, \dots, \mathbf{X}_Q$. Assume that all of the replicas are infinitely far apart:

$$\frac{1}{|\mathbf{X}_p - \mathbf{X}_q|} = 0, \quad 1 \leq p, q \leq Q; \quad p \neq q. \quad (10)$$

This ensures that the replicas do not interact.

If we assign N electrons to each replica, then the Hamiltonian for a replica is

$$\hat{H}_q^{(N)} = \sum_{i=1}^N \left(\frac{-\nabla_i^2}{2} + v(\mathbf{r}_i - \mathbf{X}_q) + \frac{1}{2} \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right). \quad (11)$$

The N -electron ground-state wavefunction for this replica is obtained by solving the electronic Schrödinger equation:

$$\hat{H}_q^{(N)} \Psi_q^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) = E_{\text{replica}}^{(N)} \Psi_q^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N). \quad (12)$$

Note that the energy does not depend on which replica we are considering, since the energy is translationally invariant and the external potentials of the replicas are identical except for translation by $\mathbf{X}_1, \mathbf{X}_2, \dots, \mathbf{X}_Q$. The wavefunctions of the replicas are also identical up to a translation,

$$\Psi_q^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N) = \Psi_{\text{replica}}^{(N)}(\mathbf{r}_1 - \mathbf{X}_q, \dots, \mathbf{r}_N - \mathbf{X}_q). \quad (13)$$

Now, let us add P electrons to the system, where $0 \leq P \leq Q$. The Hamiltonian for the total $NQ + P$ -electron system is then

$$\hat{H}_{\text{total}}^{(NQ+P)} = \sum_{i=1}^{NQ+P} \left(\frac{-\nabla_i^2}{2} + \sum_{q=1}^Q v(\mathbf{r}_i - \mathbf{X}_q) + \frac{1}{2} \sum_{j \neq i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right). \quad (14)$$

One possible ground state wavefunction for this system would be

$$\Psi_{\text{total}}(\mathbf{r}_1 \dots \mathbf{r}_{NQ+P}) = \mathcal{A} \left(\Psi_1^{(N+1)} \Psi_2^{(N+1)} \dots \Psi_P^{(N+1)} \Psi_{P+1}^{(N)} \Psi_{P+2}^{(N)} \dots \Psi_Q^{(N)} \right). \quad (15)$$

(\mathcal{A} is the antisymmetrizer.) This wavefunction assigns $N + 1$ electrons to the replicas centered at the first P locations ($\mathbf{X}_1, \dots, \mathbf{X}_P$) and N electrons to the next $Q - P$ replicas. This is a ground-state wavefunction for the system consisting of Q replicas and P extra electrons, and the energy of this wavefunction is clearly

$$E_{\text{total}} = E_1^{(N+1)} + E_2^{(N+1)} + \dots + E_P^{(N+1)} + E_{P+1}^{(N)} + \dots + E_Q^{(N)}. \quad (16)$$

Because the replicas are identical except for the number of electrons, we have

$$E_{\text{total}} = P E_{\text{replica}}^{(N+1)} + (Q - P) E_{\text{replica}}^{(N)}. \quad (17)$$

Assigning the extra electrons to the first P replicas is, of course, arbitrary. Instead of using equation (15), one can sum over all possible ways of assigning $N + 1$ electrons to P replicas and N electrons to the remaining $Q - P$ replicas. Thus

$$\begin{aligned} & \Psi_{\text{tot, sym}}(\mathbf{r}_1 \dots \mathbf{r}_{QN+P}) \\ &= \mathcal{A} \left(\sqrt{\frac{(Q - P)! P!}{Q!}} \sum_{\substack{\kappa_1, \kappa_2, \dots, \kappa_Q = \{0, 1\} \\ \kappa_1 + \kappa_2 + \dots + \kappa_Q = P}} \Psi_1^{(N+\kappa_1)} \Psi_2^{(N+\kappa_2)} \dots \Psi_Q^{(N+\kappa_Q)} \right). \end{aligned} \quad (18)$$

This is also one of the degenerate ground-state wavefunctions for the system. This wavefunction treats all the replicas the same way and is thus symmetric with respect to exchange of the coordinates of the replicas. When the supermolecule is in the state described by equation (18), all of the replicas have the same properties. Thus, the number of electrons in each replica must be $(\frac{1}{Q})$ th of the total number of electrons. That is,

$$N_1 = N_2 = \dots = N_Q = \frac{QN + P}{Q} = N + \frac{P}{Q}. \quad (19)$$

Similarly, the energy of each replica must be $(\frac{1}{Q})$ th of the total energy. Using equation (17), we have that

$$E_1 = E_2 = \dots = E_Q = \frac{P}{Q} E_{\text{replica}}^{(N+1)} + \left(1 - \frac{P}{Q}\right) E_{\text{replica}}^{(N)}. \quad (20)$$

The total density of the system is

$$\rho_{\text{tot}}(\mathbf{r}) = \sum_{q=1}^Q \left[\left(1 - \frac{P}{Q}\right) \rho_{\text{replica}}^{(N)}(\mathbf{r} - \mathbf{X}_q) + \frac{P}{Q} \rho_{\text{replica}}^{(N+1)}(\mathbf{r} - \mathbf{X}_q) \right], \quad (21)$$

where $\rho_{\text{replica}}^{(N)}(\mathbf{r} - \mathbf{X}_q)$ is the ground-state density for the N -electron system centered at \mathbf{X}_q . In general, this sort of relationship holds for any observable that is size consistent.

Two wavefunctions, Φ_p and Φ_q , are said to be strongly disjoint wavefunctions if at any place, \mathbf{x}_{i_q} , where $\Phi_q(\mathbf{x}_1, \mathbf{r}_2, \dots, \mathbf{x}_{i_q}, \dots, \mathbf{r}_{N_q})$ is not equal to zero, $\Phi_p(\mathbf{x}_1, \mathbf{r}'_2, \dots, \mathbf{x}_{i_q}, \dots, \mathbf{r}'_{N_p})$ equals zero. This implies that

$$\Phi_p^*(\mathbf{x}_1, \mathbf{r}'_2, \dots, \mathbf{r}'_{N_p}) \hat{a}(\mathbf{x}_1) \Phi_q(\mathbf{x}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_q}) = 0 \quad (22)$$

at every point in space for any operator, $\hat{a}(\mathbf{x}_1)$, with finite norm. Equation (22) is satisfied any time the wavefunctions are localized in regions of space that are infinitely far apart; it is the natural generalization of the concept of strong orthogonality [26],

$$\int \Phi_p(\mathbf{x}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_p}) \Phi_q(\mathbf{x}_1, \mathbf{r}'_2, \dots, \mathbf{r}'_{N_p}) d\mathbf{x}_1 = 0. \quad (23)$$

If two electronic systems are infinitely far apart, then the eigenfunctions of those systems are strongly disjoint. (Strictly speaking, this applies only to bound states of the subsystems; the results for continuum states may be more complicated.)

The formula for the properties of an individual replica is now derived. Consider a simple one-electron operator,

$$\hat{A}_{\text{total}} = \sum_{i=1}^{QN+P} \hat{a}(\mathbf{r}_i). \quad (24)$$

Because the wavefunctions of the replicas are strongly disjoint, integrals between N -electron wave functions on different centers vanish:

$$\begin{aligned} \int (\Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}, \mathbf{x}_N))^* \hat{a}(\mathbf{x}_N) \Psi_q^{(N)}(\mathbf{x}_N, \mathbf{r}_{N+1}, \dots, \mathbf{r}_{2N-1}) d\mathbf{x}_N &= 0, \\ \int (\Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_{N-2}, \mathbf{x}_{N-1}, \mathbf{x}_N))^* \hat{a}(\mathbf{x}_N) \Psi_q^{(N)}(\mathbf{x}_{N-1}, \mathbf{x}_N, \mathbf{r}_{N+1}, \dots, \mathbf{r}_{2N-2}) d\mathbf{x}_N &= 0, \\ &\vdots \end{aligned} \quad (25)$$

$$\int (\Psi_p^{(N)}(\mathbf{x}_1, \dots, \mathbf{x}_N))^* \hat{a}(\mathbf{x}_N) \Psi_q^{(N)}(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_N = 0.$$

Integrals between N -electron wavefunctions and $N+1$ -electron wavefunctions also vanish:

$$\begin{aligned} \int (\Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{x}_N))^* \hat{a}(\mathbf{x}_N) \Psi_q^{(N+1)}(\mathbf{x}_N, \mathbf{r}_{N+1}, \dots, \mathbf{r}_{2N}) d\mathbf{x}_N &= 0, \\ \int (\Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_{N-2}, \mathbf{x}_{N-1}, \mathbf{x}_N))^* \hat{a}(\mathbf{x}_N) \Psi_q^{(N+1)}(\mathbf{x}_{N-1}, \mathbf{x}_N, \mathbf{r}_{N+1}, \dots, \mathbf{r}_{2N-1}) d\mathbf{x}_N &= 0, \\ &\vdots \end{aligned} \quad (26)$$

$$\int (\Psi_p^{(N)}(\mathbf{x}_1, \dots, \mathbf{x}_N))^* \hat{a}(\mathbf{x}_N) \Psi_q^{(N+1)}(\mathbf{x}_1, \dots, \mathbf{x}_{N+1}) d\mathbf{x}_N = 0.$$

These identities imply that “cross terms” between different disjoint systems vanish, so that

$$\begin{aligned} & \left\langle \Psi_{\text{tot, sym}}(\mathbf{r}_1 \cdots \mathbf{r}_{Q_{N+P}}) \middle| \hat{A} \middle| \Psi_{\text{tot, sym}}(\mathbf{r}_1 \cdots \mathbf{r}_{Q_{N+P}}) \right\rangle \\ &= \frac{(Q-P)!P!}{Q!} \sum_{\substack{\kappa_1, \kappa_2, \dots, \kappa_Q = \{0,1\} \\ \kappa_1 + \kappa_2 + \dots + \kappa_Q = P}} \sum_{q=1}^Q \left\langle \Psi_q^{(N+\kappa_q)} \middle| \sum_{i=1}^{N+\kappa_q} \hat{a}(\mathbf{r}_i) \middle| \Psi_q^{(N+\kappa_q)} \right\rangle. \end{aligned} \quad (27)$$

This indicates that the value of a property for a composite system formed from Q disjoint, noninteracting subsystems is the sum of the values of that property for the subsystems.

The results for two-electron operators are similar. In analogy to equation (8), one must have electrons that are infinitely far apart do not interact, that is:

$$\lim_{|\mathbf{r}_i - \mathbf{r}_j|} \hat{a}(\mathbf{r}_i, \mathbf{r}_j) = 0. \quad (28)$$

With this result, the interactions between electrons on different systems are zero:

$$\begin{aligned} & \int \left[\left(\Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}, \mathbf{x}_N) \Psi_q^{(N)}(\mathbf{x}_{N+1}, \mathbf{r}_{N+2}, \dots, \mathbf{r}_{2N}) \right)^* \right. \\ & \quad \left. \times \hat{a}(\mathbf{x}_N, \mathbf{x}_{N+1}) \Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}, \mathbf{x}_N) \Psi_q^{(N)}(\mathbf{x}_{N+1}, \mathbf{r}_{N+2}, \dots, \mathbf{r}_{2N}) \right] d\mathbf{x}_N d\mathbf{x}_{N+1} = 0, \\ & \int \left[\left(\Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}, \mathbf{x}_N) \Psi_q^{(N+1)}(\mathbf{x}_{N+1}, \mathbf{r}_{N+2}, \dots, \mathbf{r}_{2N+1}) \right)^* \right. \\ & \quad \left. \times \hat{a}(\mathbf{x}_N, \mathbf{x}_{N+1}) \Psi_p^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_{N-1}, \mathbf{x}_N) \Psi_q^{(N+1)}(\mathbf{x}_{N+1}, \mathbf{r}_{N+2}, \dots, \mathbf{r}_{2N+1}) \right] d\mathbf{x}_N d\mathbf{x}_{N+1} = 0. \end{aligned} \quad (29)$$

This result can be easily extended to operators depending on larger numbers of electrons, but only one- and two-electron operators are commonly considered in quantum chemistry.

The quantum mechanical operator for the supermolecule can be constructed from the quantum mechanical operators of its infinitely separated replicas. The easiest way to do this is to define nonoverlapping regions of space associated with each replica, $\{\Omega_q\}_{q=1}^Q$. One then defines the one-electron operators for a replica so that they do not affect the other portions of the supermolecule:

$$\hat{a}_{\Omega_q}(\mathbf{r}_i) = \begin{cases} \hat{a}_q(\mathbf{r}_i), & \mathbf{r}_i \in \Omega_q, \\ 0, & \mathbf{r}_i \notin \Omega_q. \end{cases} \quad (30)$$

Two electron operators are defined similarly, with

$$\hat{a}_{\Omega_q}(\mathbf{r}_i, \mathbf{r}_j) = \begin{cases} \hat{a}_q(\mathbf{r}_i, \mathbf{r}_j), & \mathbf{r}_i, \mathbf{r}_j \in \Omega_q, \\ 0, & \mathbf{r}_i \notin \Omega_q, \\ 0, & \mathbf{r}_j \notin \Omega_q. \end{cases} \quad (31)$$

The quantum mechanical operator for the supermolecule is then the sum of the operators for all the replicas,

$$\hat{A}_{\text{total}} = \sum_{i=1}^{QN+P} \sum_{q=1}^Q \hat{a}_{\Omega_q}(\mathbf{r}_i) + \frac{1}{2} \sum_{i=1}^{QN+P} \sum_{j \neq i} \sum_{q=1}^Q \hat{a}_{\Omega_q}(\mathbf{r}_i, \mathbf{r}_j). \quad (32)$$

With this definition of the properties of the supermolecule, the properties of the supermolecule is always the sum of the properties of the replicas,

$$A_{\text{total}} = \sum_{q=1}^Q A_q. \quad (33)$$

If, as before, the replicas are chosen to be identical, then by the same argument that was used for the energy, one has that

$$A_1 = A_2 = \dots = A_Q = \frac{P}{Q} A_{\text{replica}}^{(N+1)} + \left(1 - \frac{P}{Q}\right) A_{\text{replica}}^{(N)}. \quad (34)$$

Equation (33) is usually discussed in the context of *size consistency*. For a size consistent system, the properties of a supermolecule are obtained by adding together the the properties of the subsystems. Mathematically:

The property A is said to be size consistent if, for a supermolecule that comprises Q infinitely separated subsystems with wavefunctions $\Phi_1, \Phi_2, \dots, \Phi_Q$, the total value of the property in the supermolecule is the sum of the values of the properties in the subsystems, as in equation (33).

Conceptually, if a property is size consistent, then it is “local.” That is, given a molecule, the size-consistent properties of that molecule do not depend on other electronic systems that are infinitely far away. For example, if one chooses the external potential of a Neon atom located at the origin to be

$$v_{\text{Ne}}(\mathbf{r}) = -\frac{10}{r} \quad (35)$$

then the electron–nuclear attraction energy is size consistent. However, if one chooses the external potential to be

$$v_{\text{Ne}}(\mathbf{r}) = -\frac{10}{r} + k \quad (36)$$

then the electron–nuclear attraction energy is not size consistent. For example, adding a Helium atom infinitely far from the Neon atom would change the electron–nuclear attraction energy by $2k$ —shifting the energy upwards k units for each electron in the Helium atom. This nonphysical behavior occurs because $v_{\Omega_{\text{Ne}}}(\mathbf{r}) = v_{\text{Ne}}(\mathbf{r})$ if one uses equation (35) for the external potential, but

not if one uses equation (36). There are also chemically important examples of nonsize-consistent operators. For example, the moments of the electron density,

$$\mu_{k_x k_y k_z} = \int (x - x_0)^{k_x} (y - y_0)^{k_y} (z - z_0)^{k_z} \rho(\mathbf{r}) d\mathbf{r} \quad (37)$$

are not size consistent unless $k_x, k_y, k_z \leq 0$. In fact, these moments are usually infinity for a supermolecule, because the function $(x - x_0)^{k_x} (y - y_0)^{k_y} (z - z_0)^{k_z}$ diverges asymptotically whenever any of the exponents are positive. This reflects the fact that the moments of the electron density are *not* size consistent: if one takes a molecule and replicates it Q times over, then the moments of the supra-molecular electron density are not simply the sums of the moments of the individual replicas. Computing molecular multipole moments using the replication method requires using the atom-truncated operator defined through equation (30) and using a different center (x_0, y_0, z_0) , for the moment expression in each replica.

2.3. *Mathematical details: irrational electron number*

The preceding analysis defines the energy and other properties of systems with rational numbers of electrons, $N + \frac{P}{Q}$, where N , P , and Q are all integers and $P \leq Q$. The analysis is readily extended to irrational numbers of electrons, however. For simplicity, let us first consider the case of three replicas with one surplus electron. ($Q = 3$; $P = 1$.) The symmetric form of the ground-state wavefunction is

$$\Psi_{\text{tot, sym}} = \mathcal{A} \left(\sqrt{\frac{1}{3}} \begin{pmatrix} \Psi_1^{(N+1)} \Psi_2^{(N)} \Psi_3^{(N)} \\ + \Psi_1^{(N)} \Psi_2^{(N+1)} \Psi_3^{(N)} \\ + \Psi_1^{(N)} \Psi_2^{(N)} \Psi_3^{(N+1)} \end{pmatrix} \right). \quad (38)$$

Another one of the degenerate ground-state wavefunction has the form:

$$\Psi_{\text{tot, } \varepsilon} = \mathcal{A} \left(\sqrt{\frac{1}{3}} \begin{pmatrix} (\sqrt{1 + \varepsilon}) \Psi_1^{(N+1)} \Psi_2^{(N)} \Psi_3^{(N)} \\ + (\sqrt{1 - \varepsilon}) \Psi_1^{(N)} \Psi_2^{(N+1)} \Psi_3^{(N)} \\ + \Psi_1^{(N)} \Psi_2^{(N)} \Psi_3^{(N+1)} \end{pmatrix} \right), \quad (39)$$

where $0 \leq \varepsilon \leq 1$. This state corresponds to a situation where the first replica has $N + \frac{1+\varepsilon}{3}$ electrons, the second replica has $N + \frac{1-\varepsilon}{3}$ electrons, and the third replica

has $N + \frac{1}{3}$ electrons. Clearly this general construction can be readily extended to additional replicas. If one does so, then one obtains the energy expression:

$$\begin{aligned} E_{\text{total}} &= P E_{\text{replica}}^{(N+1)} + (Q - P) E_{\text{replica}}^{(N)} \\ &= (Q - 2) E_{\text{replica}}^{\left(N + \frac{P}{Q}\right)} + E_{\text{replica}}^{\left(N + \frac{P+\varepsilon}{Q}\right)} + E_{\text{replica}}^{\left(N + \frac{P-\varepsilon}{Q}\right)}. \end{aligned} \quad (40)$$

Because ε can be an irrational number, this provides some information about the energy of a system with an irrational number of electrons, specifically, that

$$\begin{aligned} E_{\text{replica}}^{\left(N + \frac{P+\varepsilon}{Q}\right)} + E_{\text{replica}}^{\left(N + \frac{P-\varepsilon}{Q}\right)} &= 2 E_{\text{replica}}^{\left(N + \frac{P}{Q}\right)} \\ &= 2 \left(\frac{P}{Q} E_{\text{replica}}^{(N+1)} + \left(1 - \frac{P}{Q}\right) E_{\text{replica}}^{(N)} \right) \end{aligned} \quad (41)$$

When ε is a rational number, this equation agrees with the results in Ref. [7].

Equation (41) expresses the fact that when $N \leq N + \frac{P}{Q} - \delta \leq N + \frac{P}{Q} \leq N + \frac{P}{Q} + \delta \leq N + 1$, then the average energy the systems with $N + \frac{P}{Q} + \delta$ and $N + \frac{P}{Q} - \delta$ electrons is equal to the energy of the system with the average number of electrons, i.e.,

$$\frac{E_{\text{replica}}^{\left(N + \frac{P}{Q} + \delta\right)} + E_{\text{replica}}^{\left(N + \frac{P}{Q} - \delta\right)}}{2} = E_{\text{replica}}^{\left(N + \frac{P}{Q}\right)}. \quad (42)$$

This is true for both rational and irrational values of δ as long as $N + \frac{P}{Q} + \delta \leq N + 1$ and $N + \frac{P}{Q} - \delta \geq N$.

Equation (42) is a useful relation for the sum of the energies of two states with different numbers of electrons. For systems with a rational number of electrons, there is also a result for the difference in energy between two states with different numbers of electrons, namely

$$\frac{E_{\text{replica}}^{\left(N + \frac{P}{Q}\right)} - E_{\text{replica}}^{\left(N + \frac{P'}{Q'}\right)}}{\frac{P}{Q} - \frac{P'}{Q'}} = E_{\text{replica}}^{(N+1)} - E_{\text{replica}}^{(N)}. \quad (43)$$

This follows directly from equation (20) and expresses the fact that a plot of energy versus electron number is a collection of straight line segments (at least for rational numbers of electrons).

There is an analogous result for irrational numbers of electrons. Motivated by the form of equation (43), consider a number of electrons, $N + \frac{P'}{Q'} + \delta'$, between

the rational numbers $N + \frac{P'}{Q'}$ and $N + \frac{P}{Q}$. Define the distance between this number and $N + \frac{P}{Q}$ as

$$\delta = N + \frac{P}{Q} - \left(N + \frac{P'}{Q'} + \delta' \right) \tag{44}$$

so that

$$\begin{aligned} N &\leq N + \frac{P'}{Q'} - \delta' \leq N + \frac{P'}{Q'} \\ &\leq N + \frac{P'}{Q'} + \delta' = N + \frac{P}{Q} - \delta \\ &\leq N + \frac{P}{Q} \leq N + \frac{P}{Q} + \delta \\ &\leq N + 1. \end{aligned} \tag{45}$$

Analogous to equation (42), one has

$$\frac{E_{\text{replica}}^{(N + \frac{P'}{Q'} + \delta')} + E_{\text{replica}}^{(N + \frac{P'}{Q'} - \delta')}}{2} = E_{\text{replica}}^{(N + \frac{P'}{Q'})}. \tag{46}$$

Subtracting equation (46) from equation (42) and using equation (44) implies that

$$\frac{E_{\text{replica}}^{(N + \frac{P}{Q} + \delta)} - E_{\text{replica}}^{(N + \frac{P'}{Q'} - \delta')}}{2} = E_{\text{replica}}^{(N + \frac{P}{Q})} - E_{\text{replica}}^{(N + \frac{P'}{Q'})}. \tag{47}$$

Dividing both sides by $\frac{P}{Q} - \frac{P'}{Q'}$ and noting that $\frac{P}{Q} - \frac{P'}{Q'} = \delta + \delta'$ (cf. equation (44)), one has that

$$\begin{aligned} \frac{E_{\text{replica}}^{(N + \frac{P}{Q} + \delta)} - E_{\text{replica}}^{(N + \frac{P'}{Q'} - \delta')}}{\frac{P}{Q} + \delta - \left(\frac{P'}{Q'} - \delta' \right)} &= \frac{E_{\text{replica}}^{(N + \frac{P}{Q})} - E_{\text{replica}}^{(N + \frac{P'}{Q'})}}{\frac{P}{Q} - \frac{P'}{Q'}} \\ &= E_{\text{replica}}^{(N+1)} - E_{\text{replica}}^{(N)}. \end{aligned} \tag{48}$$

The second line in this expression follows from equation (43). When δ and δ' are rational numbers, this equation is equivalent to (43). When δ and δ' are irrational numbers, this equation indicates that the slope of the E versus N curve is the same for rational and irrational numbers.

Combined with equation (42), this actually implies that the energy is a continuous function of the electron number. To see this, note that because the E versus N curve has the slope $E_{\text{replica}}^{(N+1)} - E_{\text{replica}}^{(N)}$, then

$$E_{\text{replica}}^{\left(N+\frac{P}{Q}+\delta\right)} = E_{\text{replica}}^{\left(N+\frac{P}{Q}-\delta\right)} + 2\delta \left(E_{\text{replica}}^{(N+1)} - E_{\text{replica}}^{(N)}\right). \quad (49)$$

Inserting this into equation (42) gives:

$$\begin{aligned} E_{\text{replica}}^{\left(N+\frac{P}{Q}-\delta\right)} &= E_{\text{replica}}^{\left(N+\frac{P}{Q}\right)} - \delta \left(E_{\text{replica}}^{(N+1)} - E_{\text{replica}}^{(N)}\right) \\ &= \left(\frac{P}{Q} - \delta\right) E_{\text{replica}}^{(N+1)} + \left(1 - \left(\frac{P}{Q} - \delta\right)\right) E_{\text{replica}}^{(N)}. \end{aligned} \quad (50)$$

This equation is the direct generalization of equation (20) to irrational numbers. Since δ can be either rational or irrational, we can simplify this expression to

$$E_{\text{replica}}^{(N+\delta)} = \delta E_{\text{replica}}^{(N+1)} + (1 - \delta) E_{\text{replica}}^{(N)}, \quad (51)$$

where $0 \leq \delta \leq 1$. This establishes that the “straight line” result for the energy versus the number of electrons is valid not only for rational numbers of electrons, but also for irrational numbers of electrons. It also establishes that the energy is a continuous function of the number of electrons. Moreover, the derivative of the energy (the chemical potential) [12] is piecewise constant, with discontinuities at integer electron number.

3. Chemical reactivity indicators

The previous section established that the energy is a continuous function of the number of electrons and can be described by the expression

$$E_{\text{replica}}^{(N+x)} = x E_{\text{replica}}^{(N+1)} + (1 - x) E_{\text{replica}}^{(N)}, \quad x \in [0, 1], \quad (52)$$

where x is any real number between zero and one, inclusive. This result can clearly be extended to apply to any size-consistent property of the system:

$$A_{\text{replica}}^{(N+x)} = x A_{\text{replica}}^{(N+1)} + (1 - x) A_{\text{replica}}^{(N)}, \quad x \in [0, 1]. \quad (53)$$

Size-consistent properties are also continuous with respect to electron number.

The dependence of the energy and other properties on the number of electrons has received the greatest scrutiny in the DFT of chemical reactivity, which is often called “conceptual DFT” [8–11]. When two molecules approach, they perturb each other. If those perturbations are energetically favorable (or at least not especially unfavorable), then a chemical reaction is likely to

occur. In this way, the chemical reactivity preferences of a molecule can be predicted by studying how a molecule's energy responds to various perturbations (which are chosen to model the approach of different reagents) [11, 20, 27–30]. Response functions of the energy emerge as natural reactivity indicators.

In the DFT of chemical reactivity, one ordinarily focuses on how the molecular energy changes with respect to changes in the external potential (due to the approach of an attacking reagent) and changes in the number of electrons (due to electron transfer to/from an attacking reagent). For a system with a nondegenerate ground state, the changes with respect to the external potential can be obtained using simple perturbation theory. The first-order change is the electron density:

$$\rho^{(N)}(\mathbf{r}) = \left(\frac{\delta E^{(N)}}{\delta v(\mathbf{r})} \right)_N \quad (54)$$

and the second-order change is the linear-response (or polarizability) kernel,

$$P^{(N)}(\mathbf{r}, \mathbf{r}') = \left(\frac{\delta^2 E^{(N)}}{\delta v(\mathbf{r}') \delta v(\mathbf{r})} \right)_N = \left(\frac{\delta^2 \rho^{(N)}(\mathbf{r})}{\delta v(\mathbf{r}')} \right)_N. \quad (55)$$

Higher order response functions are rarely considered. When they need to be considered, they should probably be treated using “path integral” formulae [11, 27].

Density functional reactivity theory is usually used to describe acid/base chemistry, and its greatest successes have come from describing regioselectivity in acid/base reactions [17, 18, 31], the electronegativity equalization principle [12, 32], and the Hard/Soft Acid/Base principle [33–39]. Indeed, one may argue that the *only* convincing explanations of the electronegativity equalization principle and the Hard/Soft Acid/Base principles use DFT-based arguments. The DFT perspective is also useful when orbital relaxation or electron correlation plays a decisive role in the chemical reactivity profile of a reagent [40–43], because in those cases arguments based on conventional molecular-orbital and valence-bond theory tend to fail.

When using DFT to describe acid/base chemistry, the role of electron transfer is critical and cannot be neglected. This requires determining how the energy, electron density, and linear response kernel depend on the number of electrons. The appropriate expressions are readily obtained using equations (52) and (53). If $N \geq 1$ is assumed to be the integer number of electrons closest to the number of electrons of interest, then the energy has the expression:

$$E^{(N+x)} = \begin{cases} -x E^{(N-1)} + (1+x) E^{(N)}, & -1 \leq x \leq 0, \\ (1-x) E^{(N)} + x E^{(N+1)}, & 0 \leq x \leq 1. \end{cases} \quad (56)$$

The electron density and the linear response kernels are size-consistent properties, and so there are similar forms for these properties:

$$\rho^{(N+x)}(\mathbf{r}) = \begin{cases} -x\rho^{(N-1)}(\mathbf{r}) + (1+x)\rho^{(N)}(\mathbf{r}), & -1 \leq x \leq 0, \\ (1-x)\rho^{(N)}(\mathbf{r}) + x\rho^{(N+1)}(\mathbf{r}), & 0 \leq x \leq 1, \end{cases} \quad (57)$$

$$P^{(N+x)}(\mathbf{r}; \mathbf{r}') = \begin{cases} -xP^{(N-1)}(\mathbf{r}; \mathbf{r}') + (1+x)P^{(N)}(\mathbf{r}; \mathbf{r}'), & -1 \leq x \leq 0, \\ (1-x)P^{(N)}(\mathbf{r}; \mathbf{r}') + xP^{(N+1)}(\mathbf{r}; \mathbf{r}'), & 0 \leq x \leq 1. \end{cases} \quad (58)$$

In order to describe how these properties change when an electron donor or an electron acceptor approaches the molecule, one differentiates with respect to the number of electrons. The derivative of the energy with respect to electron number is the electronic chemical potential [5, 12]:

$$\begin{aligned} \mu^{(N+x)} &= \left(\frac{\partial E^{(M)}}{\partial M} \right)_{v(\mathbf{r}); M=N+x}, \\ \mu^{(N+x)} &= \begin{cases} \mu^- = E^{(N-1)} - E^{(N)}, & -1 \leq x \leq 0, \\ \mu^+ = E^{(N)} - E^{(N+1)}, & 0 \leq x \leq 1. \end{cases} \end{aligned} \quad (59)$$

Note that when the number of electrons is an integer ($x = 0$), the derivative does not exist. The derivative from above (μ^+) and the derivative from below (μ^-) must be used instead.

The derivative of the electron density with respect to the number of electrons is the Fukui function [17–19].

$$\begin{aligned} f^{(N+x)}(\mathbf{r}) &= \left(\frac{\partial \rho^{(M)}(\mathbf{r})}{\partial M} \right)_{v(\mathbf{r}); M=N+x}, \\ f^{(N+x)}(\mathbf{r}) &= \begin{cases} f^-(\mathbf{r}) = \rho^{(N)}(\mathbf{r}) - \rho^{(N-1)}(\mathbf{r}), & -1 \leq x \leq 0, \\ f^+(\mathbf{r}) = \rho^{(N+1)}(\mathbf{r}) - \rho^{(N)}(\mathbf{r}), & 0 \leq x \leq 1. \end{cases} \end{aligned} \quad (60)$$

The Fukui function is a key indicator of regioselectivity. The derivatives of the polarizability kernel are similarly obtained.

These formulas can be written more compactly using the Heaviside step function,

$$\Theta(x) = \begin{cases} 0, & x < 0, \\ 1, & x > 0. \end{cases} \quad (61)$$

The chemical potential can then be written as

$$\mu^{(N+x)} = \mu^- + \Theta(x)(\mu^+ - \mu^-), \quad -1 \leq x \leq 1. \quad (62)$$

Similarly, the Fukui function can be written as

$$f^{(N+x)}(\mathbf{r}) = f^-(\mathbf{r}) + \Theta(x)(f^+(\mathbf{r}) - f^-(\mathbf{r})), \quad -1 \leq x \leq 1. \quad (63)$$

These expressions are especially useful when higher-order derivatives with respect to the number of electrons need to be taken.

The second derivative of the energy with respect to the number of electrons is the chemical hardness [14],

$$\eta = \left(\frac{\partial^2 E^{(M)}}{\partial M^2} \right)_{v(r)}, \quad (64)$$

which is the key concept underlying the Hard/Soft Acid/Base [33–39] and Maximum Hardness Principles [16, 20, 44]. The derivative of the Heaviside function is the Dirac delta function:

$$\Theta(x) = \int_0^x \delta(y) dy, \quad (65)$$

$$\frac{d\Theta(x)}{dx} = \delta(x).$$

Using this relation, one finds the following expression for the chemical hardness

$$\begin{aligned} \eta^{(N+x)} &= \left(E^{(N+1)} - 2E^{(N)} + E^{(N-1)} \right) \delta(x), \quad -1 \leq x \leq 1, \\ &= (\mu^+ - \mu^-) \delta(x). \end{aligned} \quad (66)$$

The replica model advocated in this paper helps explain why systems with noninteger electron number have zero hardness: applying an infinitesimal perturbation will break the degeneracy between the replicas in the supermolecule, inducing electron transfer from the replicas that were destabilized by the perturbation to the replicas that were stabilized by the perturbation. This extreme instability is associated with zero hardness and infinite polarizability.

In recent months, there has been a large amount of interest in the second derivative of the density with respect to electron number,

$$\Delta f^{(M)}(\mathbf{r}) = \left(\frac{\partial^2 \rho^{(M)}(\mathbf{r})}{\partial M^2} \right)_{v(r)}. \quad (67)$$

This “dual descriptor” for describing chemical reactions seems to play a key role in describing reactions that are difficult to describe using electrostatic or electron transfer effects [45–47]. For example, the “dual descriptor” can be used to describe the Woodward–Hoffmann rules [47, 48] and the preference for the endo or exo conformers in Diels–Alder reactions [49]. The dual descriptor can be computed using a formula analogous to equation (66),

$$\begin{aligned} \Delta f^{(N+x)}(\mathbf{r}) &= \left(\rho^{(N+1)}(\mathbf{r}) - 2\rho^{(N)}(\mathbf{r}) + \rho^{(N-1)}(\mathbf{r}) \right) \delta(x), \quad -1 \leq x \leq 1, \\ &= \left(f^+(\mathbf{r}) - f^-(\mathbf{r}) \right) \delta(x). \end{aligned} \quad (68)$$

Equations (66) and (68) for the hardness and the dual descriptor are the basis for many practical computational schemes, although the δ -function dependence is typically ignored. When the δ -function dependence is ignored one is effectively “smoothing over” the derivative discontinuity with respect to the number of electrons.

Except for the equation for the dual descriptor, equation (68), all of these results can be found in the literature. In most cases, the results were known to the research community long before they ever appeared in print. For example, the equations for the Fukui function, equation (60), were certainly known in 1982 [5], although an explicit statement expressing the fact that “the finite difference approximation is exact” seems not to appear until much later, in a review article [19].

4. Discussion

Section 2 of this paper establishes the “linear mixing rule” for noninteger number of electrons,

$$A_{\text{replica}}^{(N+\delta)} = x A_{\text{replica}}^{(N+1)} + (1-x) A_{\text{replica}}^{(N)}, \quad 0 \leq x \leq 1 \quad (69)$$

and size-consistent properties, A . This extends the analysis in Ref. [7], which focused on the energy and addressed only the case where x was a rational number. The extension to other size-consistent properties is not unexpected (indeed, it is implicit in many previous treatments). The extension to irrational numbers of electrons is an interesting mathematical exercise, but the results are just as one would expect: there is no reason to expect that a system’s properties would toggle between qualitatively different values based solely on whether the total number of electrons was rational or irrational. The major contribution of section 2, then, is to “tie up” of some loose mathematical ends left behind in Ref. [7]. The most important “loose end” is to prove the continuity of the energy (and other size consistent properties) with respect to the number of electrons. In fact, molecular properties are linear functions of electron number *except* for integer numbers of electrons. This smoothness allows one to differentiate properties with respect to the number of electrons, as is commonly done in the density functional theory of chemical reactivity.

In section 3, formulas for chemical reactivity indicators are derived. None of these results is unexpected, and results of this sort have appeared scattered throughout the literature, though most of those formulas were derived by taking the zero temperature limit of the grand canonical ensemble. The present approach is more direct, less error prone, and probably more instructive. Occasionally people ask whether it is acceptable to choose an ansatz in which there are no derivative discontinuities. Based on this analysis, the answer is “no.” While one may argue that the zerotemperature grand canonical ensemble

is an *ad hoc* construction for fractional electron number, no such objection can be raised to the present construction. One can construct an ansatz where molecular properties do not vary in the piecewise linear fashion expressed in equation (69), but it requires defining the properties with nonsize-consistent operators. If one uses nonsize-consistent operators, then the properties of a molecule will depend on the properties of another molecule an infinite distance away. In this sense, “size consistency” is a choice, and not a requirement. It seems intuitively reasonable, however, to prefer theoretical approaches where the response of a molecule to accepting/donating electrons to another molecule that is infinitely far away does not depend on the identity of the other molecule.

Equations (63) and (68) seem to be new but, in light of the previous known results, these expressions are not very surprising.

When one combines the “mathematical” results in section 2 with the “chemical” results in section 3, interesting interpretations emerge. The first thing that one notices is that the analysis in section 2 is critically dependent on the size consistency of the properties under consideration. This has a simple interpretation: given a molecule, B , its properties should not change if one introduces another molecule, C , an infinite distance away. This “obvious” statement is true for size-consistent properties, but not for nonsize-consistent properties like, for example, the expectation value of the “shifted Neon” potential in equation (36). All of the indicators commonly used in density functional theoretic studies of chemical reactivity are size consistent.

Parr has emphasized that the dependence of the energy, and other properties, on the number of electrons can be likened to a phase transition [50]. The Schrödinger equation defines the properties of systems with integer numbers of electrons; these are “pure states.” If one considers the chemical potential and the external potential to be the variables that control the state of the system, then the “pure state” with N electrons is stable as long as the chemical potential is in the range

$$\mu^- < \mu < \mu^+, \quad (70)$$

where μ^- and μ^+ are the derivatives from below and above (cf. equation (59)) and are identified as minus the vertical ionization potential and minus the vertical electron affinity, respectively. If one lowers the chemical potential so that it is equal to μ^- , then a phase transition occurs and the system becomes a “mixed state” where the N -electron state is mixed with the $N - 1$ -electron state. During the phase transition, the chemical potential and the external potential are constant, and one needs an additional variable (here, the number of electrons) to describe the system and determine its properties. This is very similar to what happens in an ordinary phase diagram.

Similarly, if one uses the number of electrons and the external potential to define the states, then the size-consistent properties of the system change

smoothly (linearly!) with respect to the number of electrons until an integer number of electrons is encountered. At that point, the way the properties of the system change with respect to further decreases/increases in the number of electrons changes abruptly and discontinuously, just like the properties of a liquid change abruptly when it solidifies or vaporizes.

Finally, it should be emphasized that when one considers an atom or a molecular fragment embedded in a reacting system, the analysis presented here is not really appropriate. In those cases, the system in question interacts in a highly specific way with its surroundings, and the identity of the source/sink of the electrons that are donated to/accepted from the system is important. That is, the exact analysis presented here is most appropriate for isolated molecules and molecules in low-density environments. (Very roughly, gas phase chemistry.) For systems in condensed phases, a different approach is needed [51–55]. Exactly what that different approach should be is still a subject of debate.

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