Density-Functional Theory for Fractional Particle Number: Derivative Discontinuities of the Energy

John P. Perdew

Department of Physics and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

and

Robert G. Parr

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514

and

Mel Levy

Department of Chemistry and Quantum Theory Group, Tulane University, New Orleans, Louisiana 70118

and

Jose L. Balduz, Jr.

Department of Physics, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

The Hohenberg-Kohn theorem is extended to fractional electron number N, for an isolated open system described by a statistical mixture. The curve of lowest average energy E_N versus N is found to be a series of straight line segments with slope discontinuities at integral N. As N increases through an integer M, the chemical potential and the highest occupied Kohn-Sham orbital energy both jump from $E_M - E_{M-1}$ to $E_{M+1} - E_M$. The exchange-correlation potential $\delta E_{xc}/\delta n(\vec{r})$ jumps by the same constant, and $\lim_{r \to \infty} \delta E_{xc}/\delta n(\vec{r}) \geq 0$.

The great practical and conceptual importance of density-functional theory[1-2] is well established.[3] For a system of N electrons subject to an external potential $v(\vec{r})$, Hohenberg and Kohn[1] have demonstrated the existence of a functional $E_v[n]$ such that minimization of $E_v[n]$ with respect to variations of $n(\vec{r})$, subject to the constraint $\int d^3r\, n(\vec{r}) = N$, yields the ground-state density $n(\vec{r})$ and energy E. It is commonly supposed that number-conserving variations may be replaced by arbitrary ones through the introduction of a Lagrange multiplier μ:

$$\delta\{E_v[n] - \mu \int d^3r\, n(\vec{r})\} = 0. \tag{1}$$

The Euler-Lagrange equation for $n(\vec{r})$ is then

$$\delta E_v/\delta n(\vec{r}) = \mu, \tag{2}$$

and

$$\mu = \partial E/\partial N. \tag{3}$$

The formal similarity of Eq. (3) to the equation for the chemical potential of an open system has led to the identification of μ with the chemical potential[4] and of $\chi = -\mu$ with the electronegativity.[4,5]

Two fundamental questions lie obscured beneath Eqs. (1)–(3): (1) Is the energy E defined for nonintegral electron number N? (2) Is E differentiable with respect to N?

If the answers to both questions are yes, a paradox arises within Hohenberg-Kohn theory: Consider a system composed of two well-separated atoms X and Y in an otherwise empty universe. The system energy $E_{XY} = E_X + E_Y$ is simply the sum of the separate atomic energies. Let X and Y be different neutral atoms with different chemical potentials, $\mu_Y < \mu_X$. A density variation which shifts $\delta N_Y > 0$ electrons from X to Y will then lower the system energy: $\delta E_{XY} = (\mu_Y - \mu_X) \times \delta N_Y < 0$. The energy will minimize with a net negative charge on Y and a net positive charge on X, in contradiction of the facts.

This example suggests that fractional electron number may arise *as a time average* in an open system, e.g., atom X which is free to exchange electrons with atom Y. In quantum mechanics, an open system with a fluctuating number of particles is described not by a pure state or wave function Ψ but by a statistical mixture or ensemble Γ. The latter is defined by a set of pure states $\Psi_1, \Psi_2, \ldots$ and their respective probabilities $p_1, p_2, \ldots$; the expectation value of an operator $\hat{O}$ is $\langle \hat{O} \rangle_\Gamma = \sum_i p_i \langle \Psi_i | \hat{O} | \Psi_i \rangle$. Note that at zero temperature the system and its reservoir together may alternatively be described by a sin-

gle pure state.

We now extend the Hohenberg-Kohn theorem to trial densities $n(\vec{r})$ which integrate to $N = M + \omega$ electrons where M is a nonnegative integer and $0 \leqslant \omega \leqslant 1$. We follow the "constrained search" formulation which has already been applied to pure states[6] and to ensembles,[7] for N = fixed integer. Define the universal variational functional

$$F[n] = \min_{\Gamma \to n} \langle \hat{T} + \hat{V}_{ee} \rangle_{\Gamma} , \qquad (4)$$

where $\hat{T}$ and $\hat{V}_{ee}$ are the kinetic and electron-electron repulsion energy operators, respectively. $F[n]$ searches over all statistical mixtures Γ (of a certain allowed type) which yield the given density $n(\vec{r})$, and delivers the minimum $\langle \hat{T} + \hat{V}_{ee} \rangle_{\Gamma}$. The allowed type is a mixture of an M-electron pure state Ψ_M with an $(M+1)$-electron pure state Ψ_{M+1}. The respective probabilities must be $1 - \omega$ and ω, since $(1 - \omega)M + \omega(M+1) = M + \omega$. Note that $n(\vec{r}) = (1 - \omega)n_M(\vec{r}) + \omega n_{M+1}(\vec{r})$ [where $\Psi_M(\vec{r})$ yields the density $n_m(\vec{r})$, etc.]. More importantly, note the existence of the variational principle: Minimization of $E_v[n] \equiv F[n] + \int d^3 r n(\vec{r}) v(\vec{r})$ with respect to number-conserving variations of $n(\vec{r})$ yields the lowest average energy that can be achieved by $M + \omega$ electrons in a statistical mixture of the allowed type,

$$E = (1 - \omega)E_M + \omega E_{M+1} , \qquad (5)$$

where E_M and E_{M+1} are the ground-state energies for M and $M+1$ electrons subject to the external potential $v(\vec{r})$.

Alternatively, the constrained search of Eq. (4) may be extended over all statistical mixtures of any type yielding the density $n(\vec{r})$. The minimum of $E_v[n]$ over all $n(\vec{r})$ integrating to $M + \omega$ electrons is still Eq. (5), provided that the plot of E_M versus integer M is concave upward (as it is in ordinary electronic systems). The reader may verify this for a mixture of $(M-1)$-, M-, and $(M+1)$-electron states; the minimizing energy E is independent of the reservoir. [The concave-upward condition, $E_M < (E_{M+1} + E_{M-1})/2$, is satisfied for noninteracting fermions and enhanced by repulsive interactions.]

According to Eq. (5), the curve of E versus N is a series of straight-line segments. The curve itself is continuous, but its derivative $\mu = \partial E / \partial N$ has possible discontinuities at integral values of N. This conclusion is consistent with recent work by Phillips and Davidson,[8] who gave an analytic form for $E(N)$ for a model of harmonically interacting fermions in a harmonic external po-

tential. Assuming that this form could be extended to nonintegral N, they found discontinuities of $\mu = \partial E / \partial N$ at certain integers.

When applied to a single atom of integral nuclear charge Z, Eqs. (3) and (5) give

$$\mu = \begin{cases} -I & (Z - 1 < N < Z), \\ -A & (Z < N < Z + 1), \end{cases} \qquad (6)$$

where $I = E_{Z-1} - E_Z$ and $A = E_Z - E_{Z+1}$ are the first ionization potential and electron affinity, respectively. The functional derivative $\delta E_v / \delta n(\vec{r})$ of Eq. (2) may or may not be defined for a neutral atom, but in any case the density may be found by solving the Euler equation (2) for either $N > Z$ or $N < Z$ and then taking the limit $N \to Z$; the two limits for $\delta E_v / \delta n(\vec{r})$ will differ by the constant $I - A$.

We can now resolve the paradox with which we began. Figure 1 shows the total energy of a neutral system composed of atom X and atom Y at infinite separation, as a function of $\Delta N_X \equiv N_X - Z_X$. The energy minimizes $nonanalytically$ at $\Delta N_X = 0$ for any choice of X or Y, since the smallest first ionization potential of the periodic table ($I = 3.89$ eV for Cs) is greater than the largest electron affinity ($A = 3.62$ eV for Cl).

If the atoms are at a large $finite$ separation R, one must include the Coulomb interaction $-e^2/R$ in the energies of the ionic configurations X^+Y^- and X^-Y^+, as also shown in Fig. 1. Let

$$\chi_i^{\mathfrak{M}} = \tfrac{1}{2}(I_i + A_i) \qquad (7)$$

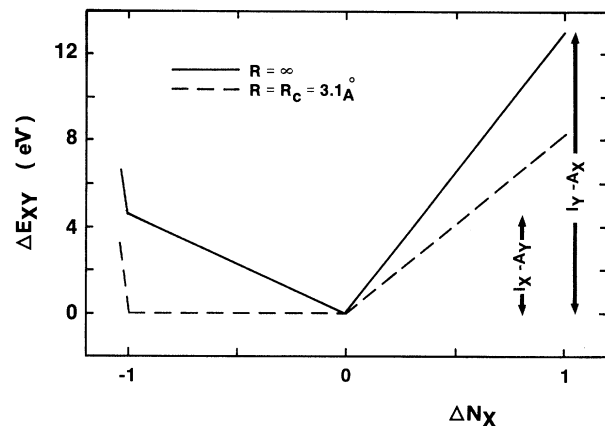be the Mulliken[9] electronegativity of neutral atom

FIG. 1. Change in total energy of two atoms X and Y, separated by a large distance R, when $\Delta N_X = N_X - Z_X$ electrons are transferred from Y to X. ($X =$ Li, $Y =$ H).

i and let Y denote the more electronegative atom. Then the ground state is the neutral-atom state $XY(\Delta N_X = 0)$ for $R > R_c$, and the singly charged ionic state $X^+Y^-(\Delta N_X = -1)$ for $R < R_c$, where the critical separation is

$$R_c = e^2(I_X - A_Y)^{-1}. \tag{8}$$

At the critical separation, large fluctuations in the charge on each atom can occur. This prediction of a sudden switch of ground-state character at a critical separation applies unequivocally to CsCl, where $R_c = 53$ Å. For LiH, where $R_c = 3.1$ Å, the prediction may fail if other interactions supervene.

Essentially, electronegativity differences among the constituent atoms determine the direction and magnitude of charge transfer upon formation of molecules and solids. That Mulliken's formula is an approximation to a slope of an E versus N curve was first pointed out by Pritchard and Sumner.[10]

At strictly zero temperature, an atom in equilibrium with a reservoir will be neutral for any chemical potential in the range $-I < \mu < -A$. We can get a sharper value by applying standard techniques of the grand canonical ensemble at *finite* temperature $T = 1/k_B\beta$. The probability of a stationary state Ψ_i is $p_i = \exp[-\beta(E_i - \mu N_i)]/\sum_j \exp[-\beta(E_j - \mu N_j)]$. For $Z - 1 < N < Z + 1$ and low T, the only nonnegligible probabilities belong to the ground states for $Z - 1$, Z, and $Z + 1$ electrons. The average energy and particle number are, respectively, $E = \sum_i p_i E_i$ and $N = \sum_i p_i N_i$. The latter equation may be solved explicitly to

find

$$\mu = -\frac{1}{\beta} \ln\left\{\frac{-\Delta + [\Delta^2 + 4e^{-\beta(I-A)}(1 - \Delta^2)]^{1/2}}{2e^{-\beta I}(1 + \Delta)}\right\}, \tag{9}$$

where $\Delta = N - Z$. μ still has the meaning of Eq. (3), with the derivative taken at constant entropy.[5] Note that

$$\mu = \begin{cases} -\infty & (N = Z - 1), \\ -\frac{1}{2}(I + A) & (N = Z), \\ +\infty & (N = Z + 1), \end{cases} \tag{10}$$

as first shown by Gyftopoulos and Hatsopoulos.[5] In particular, the chemical potential of the neutral atom is $-\chi^{\mathfrak{M}}$ where $\chi^{\mathfrak{M}}$ is the Mulliken electronegativity of Eq. (7), as expected.[4,5] Note also that as $T \to 0$ the continuous dependence of Eq. (9) upon N reduces to the discontinuous one of Eq. (6). For atoms, ordinary temperatures are quite low: On the scale of Fig. 1 the eye cannot distinguish between $T = 0$ K and $T = 2000$ K.

Similarly, consider the problem of *two* well-separated atoms, X and Y, in equilibrium with a reservoir. Let the two atoms be overall neutral: $N_X + N_Y = Z_X + Z_Y$. Then we find that as $T \to 0$

$$\mu = -\frac{1}{2}(I_{\min} + A_{\max}), \tag{11}$$

where $I_{\min}$ is the lesser of I_X and I_Y, and $A_{\max}$ the greater of A_X and A_Y. The two atoms are then separately neutral: $N_X = Z_X$ and $N_Y = Z_Y$. To prove Eq. (11), following Ref. 9, compare the energy changes for $XY + UV \to (XY)^+ + (UV)^-$ and $XY + UV \to (XY)^- + (UV)^+$.

Practical calculations within density-functional theory usually appeal to the Kohn-Sham theorem, which asserts that the density $n(\vec{r})$ and energy E may be constructed from orbitals $\psi_{\alpha\sigma}(\vec{r})$ satisfying the self-consistent Schrödinger equation

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + v(\vec{r}) + e^2 \int d^3r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}}{\delta n(\vec{r})}\right]\psi_{\alpha\sigma}(\vec{r}) = \epsilon_\alpha \psi_{\alpha\sigma}(\vec{r}), \tag{12}$$

where $E_{xc}[n]$ is the exchange-correlation energy. An extension[11,12] of the Kohn-Sham theorem applies even to an interacting system whose ground-state density is *not* also a ground-state density for *noninteracting* electrons in a local potential. The orbital energies still have the significance[13]

$$\epsilon_\alpha = \partial E / \partial f_{\alpha\sigma}, \tag{13}$$

where $f_{\alpha\sigma}$ is the occupation number of orbital $\psi_{\alpha\sigma}(\vec{r})$. The electron number may be nonintegral, and $0 \leq f_{\alpha\sigma} \leq 1$.

Exact results may now be derived for the maximum occupied Kohn-Sham orbital energy $\epsilon_{\max}$

and for the large-r limit of the Kohn-Sham potential in an atom. Comparison of Eqs. (3), (6), and (13) reveals that

$$\epsilon_{\max} = \begin{cases} -I & (Z - 1 < N < Z), \\ -A & (Z < N < Z + 1). \end{cases} \tag{14}$$

Consider what this means for, say the H atom with its degenerate $1s_\uparrow$ and $1s_\downarrow$ orbitals: As N increases through Z, the exchange-correlation potential $\delta E_{xc}/\delta n(\vec{r})$ must jump discontinuously by the constant $I - A$. Moreover, rigorous theorems on the long-range behavior[11,14] of the den-

sity in a neutral atom reveal that

$$\epsilon_{max} - v_{eff}(\infty) \leq -I , \qquad (15)$$

where $v_{eff}(\vec{r})$ is the effective potential in Eq. (12). From Eqs. (14) and (15) we can conclude that

$$v_{eff}(\infty) = \lim_{r \to \infty} \delta E_{xc} / \delta n(\vec{r}) \geq 0 . \qquad (16)$$

By Eq. (2), $\mu = \lim_{r \to \infty} \{ \delta T_s / \delta n(\vec{r}) + \delta E_{xc} / \delta n(\vec{r}) \}$ where $T_s[n]$ is the noninteracting kinetic energy,[2,11,12] and thus $\mu \geq \lim_{r \to \infty} \delta T_s / \delta n(\vec{r})$. All bounds are expected to be very tight[14] when N tends to Z from below.

The exchange-correlation functional $E_{xc}[n]$ is not known explicitly except in various approximations. For separated LiH the local density approximation[2] displays no derivative discontinuity, and so it minimizes the energy incorrectly at the configuration $Li^{+0.25}H^{-0.25}$. The spin-restricted Hartree-Fock approximation leads to an even worse dissociation limit,[15] $Li^{+0.45}H^{-0.45}$.

All of our conclusions concerning atoms may be generalized to other electronic systems. In particular, the metal-insulator transition due to correlation is another example of a derivative discontinuity of E_{xc}.

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Direct Optical Observation of Interfacial Depletion Layers in Polymer Solutions

C. Allain, D. Ausserre, and F. Rondelez

Physique de la Matière Condensée, Collège de France, F-75231 Paris Cédex 05, France

The excitation of fluorescently labeled polymer coils by shallow optical evanescent waves permits measurement of the local monomer solute concentration in the vicinity of a nonadsorbing wall over controlled, submicroscopic distances. The existence of a depletion layer at the solid-solution interface is thus demonstrated directly for the first time. The results obtained on a 103 000-molecular-weight polystyrene sample dissolved in ethyl acetate are in agreement with the entropic repulsion model.

Interfacial phenomena are a field of growing physical interest and have generated a recent outburst of experimental work in various systems.[1] In most of these cases, the results were obtained in the vicinity of a phase transition, which has the advantage of scaling up the interfacial layer thickness.

The present work is devoted to dilute macromolecular solutions in the vicinity of an impenetrable, nonadsorbing wall. Such a system is amenable to experimental investigation because of the large size of the constituent objects and is relevant to such important research fields as colloid stabilization, gel permeation chromatography,

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