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LETTER TO THE EDITOR

Extremal properties of the Harris energy functional

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Abstract. We show that the energy functional defined by Harris has a local maximum at the exact ground-state density of an electronic system provided the dielectric screening matrix of the system has eigenvalues that are all greater than unity.

Recently Harris (1985), and independently Foulkes and Haydock (1989), introduced an approximate energy functional for the calculation of ground-state electronic properties. The functional is based on the Kohn–Sham (Kohn and Sham 1965) implementation of density functional theory (Hohenberg and Kohn 1964) and was motivated by the need for simplified but accurate computational schemes for complex electronic systems. The application envisaged by Harris was to the interaction between well defined units, or fragments, such as atoms in a molecule or solid. In this sense it complements the quasi-atom (Stott and Zaremba 1980) or effective medium (Nørskov and Lang 1980) theories which focus on the energetics of an atom in an arbitrary electronic host environment. Harris' fragment formula has proved to be remarkably successful and is therefore an important addition to the arsenal of computational tools available for electronic structure calculations.

By its construction, the Harris functional is stationary about the exact ground-state density of the system but the sign of the error in the energy estimate was left undetermined. In applications to molecules (Harris 1985), the Harris functional was found to yield binding energies which were close to those of self-consistent calculations (Painter and Averill 1982) but the error was sometimes positive and sometimes negative. This comparison is somewhat inconclusive, however, since the two sets of calculations are based on slightly different energy functionals and make use of different numerical techniques. Subsequently, Polatoglou and Methfessel (1988) applied the Harris functional to the calculation of the cohesive energy of solids and almost invariably found values that exceeded (albeit slightly) their own self-consistent results. More recently, Finnis (1990) applied the method to a thin slab of aluminium and likewise obtained energies with the Harris functional that lay below the self-consistent values. In view of these results he conjectured that the Harris functional is a maximum at the exact ground-state density and therefore admits a variational principle, at least locally within the vicinity of the extremum. It is clearly imperative to establish the conditions under which the Harris functional can be used variationally. This is the problem we address in this letter. We find that the Harris functional does indeed have a local maximum at the true ground-state density, unless the electronic system possesses anomalous screening properties. A precise statement of this conclusion follows.

We first establish our notation and summarise some of the salient features of density functional theory. The energy functional defined by Hohenberg and Kohn (1964) is written as

$$E_v[n] = \int nv + F[n] \quad (1)$$

where v is an external potential acting on the electronic system. F is a universal functional of the density which can be partitioned as

$$F[n] = T[n] + \frac{1}{2} \iint \frac{nn}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n]. \quad (2)$$

The first term on the right, $T[n]$, is the kinetic energy of a *non-interacting* system of electrons with density $n(\mathbf{r})$, the second term is the classical electrostatic self-energy of the electronic charge distribution and the remainder, $E_{xc}[n]$, is by definition the exchange-correlation energy functional. We make the usual assumptions regarding the v -representability of all density distributions considered. Equation (1) also serves for a non-interacting system of fermions with the replacement of F by T .

According to the Hohenberg–Kohn theorem, $E_v[n]$ is a minimum at the true ground-state density, n^{sc} . The superscript denotes ‘self-consistent’ and is used here to indicate the connection with the usual Kohn–Sham self-consistency procedure in which $T[n]$ is given in terms of the eigenfunctions and eigenvalues of an independent particle Schrödinger equation:

$$T[n] = \sum_i \varepsilon_i - \int nv_{\text{eff}} \quad (3)$$

$$v_{\text{eff}} = v + \int \frac{n}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{xc}}{\delta n} \quad (4a)$$

$$(-\frac{1}{2}\nabla^2 + v_{\text{eff}})\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r}) \quad (4b)$$

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2. \quad (4c)$$

The effective potential, v_{eff} , is a functional of n and the set of equations (4a)–(4c) is usually solved using an iterative technique that ensures convergence to the final density n^{sc} .

More generally, n^{sc} is determined by the Euler equation

$$(\delta E_v / \delta n)|_{n^{sc}} = v + (\delta F / \delta n)|_{n^{sc}} = 0. \quad (5)$$

For small deviations of the density from n^{sc} ($\delta n = n - n^{sc}$), $E_v[n]$ can be expanded about n^{sc} with the result

$$\begin{aligned} \delta E_v[n] &\equiv E_v[n] - E_v[n^{sc}] = \frac{1}{2} \iint \left. \frac{\delta^2 F}{\delta n^2} \right|_{n^{sc}} \delta n(\mathbf{r}) \delta n(\mathbf{r}') + \dots \\ &\equiv \frac{1}{2} \iint \delta n(\mathbf{r}) K(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}'). \end{aligned} \quad (6)$$

The symmetric kernel $K(\mathbf{r}, \mathbf{r}')$ defined by this equation is a ground-state property of the electronic system. According to (2) it has the form

$$K(\mathbf{r}, \mathbf{r}') = (\delta^2 T / \delta n^2)|_{n^{\text{sc}}} + 1/|\mathbf{r} - \mathbf{r}'| + (\delta^2 E_{\text{xc}} / \delta n^2)|_{n^{\text{sc}}}. \quad (7)$$

We can similarly define

$$K_0(\mathbf{r}, \mathbf{r}') = (\delta^2 T / \delta n^2)|_{n^{\text{sc}}} \quad (8)$$

for a non-interacting system, so

$$K(\mathbf{r}, \mathbf{r}') = K_0(\mathbf{r}, \mathbf{r}') + C(\mathbf{r}, \mathbf{r}') \quad (9)$$

where

$$C(\mathbf{r}, \mathbf{r}') = 1/|\mathbf{r} - \mathbf{r}'| + (\delta^2 E_{\text{xc}} / \delta n(\mathbf{r}) \delta n(\mathbf{r}'))|_{n^{\text{sc}}} \quad (10)$$

represents an effective electron–electron interaction. By the variational principle, K is a positive definite operator in the sense that δE_v is positive for any non-trivial density fluctuation δn . K_0 also has this property since the energy functional

$$E_{v_0}^0[n] = \int n v_0 + T[n]$$

is also stationary about some density n_0 :

$$v_0 + (\delta T / \delta n)|_{n_0} = 0. \quad (11)$$

With $v_0 = v_{\text{eff}}^{\text{sc}}$, the effective potential obtained with n^{sc} , $n_0 = n^{\text{sc}}$.

The kernels defined in (7)–(10) are in fact related to density response functions. Taking the variation of (5) with respect to v we find

$$\delta v + \int \frac{\delta^2 F}{\delta n^2} \Big|_{n^{\text{sc}}} \delta n = 0 \quad (12)$$

which relates the induced density δn to the perturbation δv . Alternatively, we have by linear response theory,

$$\delta n = \int \chi \delta v \quad (13)$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is the static density response function of the system. Comparing (12) and (13) we have

$$K = -\chi^{-1} \quad (14)$$

and similarly

$$K_0 = -\chi_0^{-1}. \quad (15)$$

In terms of χ , equation (6) becomes

$$\delta E_v[n] = -\frac{1}{2} \iint \delta v(\mathbf{r}) \chi(\mathbf{r}, \mathbf{r}') \delta v(\mathbf{r}') \quad (16)$$

and so, according to these definitions, χ is negative definite.

From (9), (14) and (15) we find

$$\chi = (\chi_0^{-1} - C)^{-1} = \chi_0(1 - C\chi_0)^{-1} \equiv \chi_0 \varepsilon^{-1} \quad (17)$$

which defines the dielectric matrix

$$\varepsilon = 1 - C\chi_0. \quad (18)$$

This matrix provides a measure of the screening response of the system and plays a central role in the following discussion. We note in passing that ε is not a symmetric operator despite the fact that both χ_0 and C are.

We now consider in more detail the situation discussed by Finnis (1990). We imagine starting with some trial density n^{in} which is close to the self-consistent density n^{sc} . With this density we construct the potential $v_{\text{eff}}^{\text{in}} \equiv v_{\text{eff}}[n^{\text{in}}]$ and solve (4b) to obtain the eigenvalues $\varepsilon_i^{\text{out}}$ and density

$$n^{\text{out}} = \sum_i |\psi_i^{\text{out}}|^2.$$

The variational estimate of the energy, $\delta E_v[n^{\text{out}}]$, is obtained from (6) with $\delta n^{\text{out}} = n^{\text{out}} - n^{\text{sc}}$. On the other hand, the Harris energy functional (Harris 1985) is defined as

$$E_{\text{H}}[n^{\text{in}}] = \sum_i \varepsilon_i^{\text{out}} - \int n^{\text{in}} (\frac{1}{2} \phi^{\text{in}} + v_{\text{xc}}^{\text{in}}) + E_{\text{xc}}[n^{\text{in}}] \quad (19)$$

and its deviation from $E_v[n^{\text{out}}]$ reduces to

$$E_{\text{H}}[n^{\text{in}}] - E_v[n^{\text{out}}] = -\frac{1}{2} \iint C(\mathbf{r}, \mathbf{r}') (n^{\text{out}} - n^{\text{in}})(n^{\text{out}} - n^{\text{in}}). \quad (20)$$

This is the same result as given by Finnis (1990) but here $C(\mathbf{r}, \mathbf{r}')$ is defined at the density n^{sc} ; the difference is immaterial since it represents a higher-order correction in the deviation of the density from n^{sc} . Combining $\delta E_v[n^{\text{out}}]$ with (20) we obtain for the deviation of the Harris functional from $E_v[n^{\text{sc}}]$ the expression

$$\begin{aligned} \delta E_{\text{H}}[n^{\text{in}}] &= \frac{1}{2} \iint \delta n^{\text{out}} K \delta n^{\text{out}} - \frac{1}{2} \iint (\delta n^{\text{out}} - \delta n^{\text{in}}) K (\delta n^{\text{out}} - \delta n^{\text{in}}) \\ &+ \frac{1}{2} \iint (\delta n^{\text{out}} - \delta n^{\text{in}}) K_0 (\delta n^{\text{out}} - \delta n^{\text{in}}). \end{aligned} \quad (21)$$

We know from the variational principle that each of these integrals is positive definite; however, we are interested in the overall sign of $\delta E_{\text{H}}[n^{\text{in}}]$ and this cannot be surmised from a casual inspection of (21).

Our expressions for $\delta E_v[n^{\text{out}}]$ and $\delta E_{\text{H}}[n^{\text{in}}]$ can be shown to be identical to those derived by Finnis (1990). Using $v_0 = v_{\text{eff}}^{\text{in}}$ in (11) gives the density n^{out} . Expanding $v_{\text{eff}}^{\text{in}}$ about $v_{\text{eff}}^{\text{sc}}$ and n^{out} about n^{sc} , we find

$$\int K_0 \delta n^{\text{out}} = - \int C \delta n^{\text{in}} \quad (22)$$

which establishes the linear relationship between δn^{out} and δn^{in} . Using (22) to eliminate K_0 , we have

$$\delta E_v[n^{\text{out}}] = \frac{1}{2} \iint C(\mathbf{r}, \mathbf{r}') (n^{\text{out}} - n^{\text{sc}})(n^{\text{out}} - n^{\text{in}}) \quad (23a)$$

and from (21)

$$\delta E_{\text{H}}[n^{\text{in}}] = \frac{1}{2} \iint C(\mathbf{r}, \mathbf{r}') (n^{\text{in}} - n^{\text{sc}})(n^{\text{out}} - n^{\text{in}}). \quad (23b)$$

These equations are in the form presented by Finnis (1990) but the earlier expressions are better suited to further analysis.

We now consider equation (21) and use (22) to eliminate either δn^{in} or δn^{out} . In this way we arrive at the alternative forms

$$\delta E_{\text{H}}[n^{\text{in}}] = \frac{1}{2} \iint \delta n^{\text{in}} (K - K K_0^{-1} K) \delta n^{\text{in}} \quad (24a)$$

$$\delta E_{\text{H}}[n^{\text{in}}] = \frac{1}{2} \iint \delta n^{\text{out}} (K - K(K - K_0)^{-1} K) \delta n^{\text{out}} \quad (24b)$$

which display $\delta E_{\text{H}}[n^{\text{in}}]$ as a quadratic form. Equation (24a) is particularly informative. If we assume that δn^{in} is v -representable, we have

$$\delta v^{\text{in}} = - \int K \delta n^{\text{in}}$$

so (24a) becomes

$$\delta E_{\text{H}}[n^{\text{in}}] = \frac{1}{2} \iint \delta v^{\text{in}} (\chi_0 - \chi) \delta v^{\text{in}} = \frac{1}{2} \int (\delta n_0^{\text{in}} - \delta n^{\text{in}}) \delta v^{\text{in}}. \quad (25)$$

δn^{in} is the density induced by δv^{in} in the interacting system while δn_0^{in} is the density that would be induced by δv^{in} in a non-interacting system having the *same* density n^{sc} . On physical grounds one would expect δn_0^{in} to be larger in magnitude than δn^{in} since the repulsive Coulomb interaction between electrons will tend to inhibit the response to an external potential. In other words, the electrons screen the external fields and would therefore be expected to respond to a lesser degree. These statements are obviously imprecise since the density response is non-local however, they suggest why $\delta E_{\text{H}}[n^{\text{in}}]$ might be expected to be negative definite (note that χ and χ_0 are negative definite), implying that $E_{\text{H}}[n]$ has a local maximum at $n = n^{\text{sc}}$.

To proceed we introduce a matrix representation of the various kernels. This is done by choosing some complete set of real orthonormal functions $f_i(\mathbf{r})$, for example a discrete Fourier representation, in terms of which the density deviation can be expanded as

$$\delta n(\mathbf{r}) = \sum_i x_i f_i(\mathbf{r}). \quad (26)$$

An arbitrary quadratic form is then expressible as

$$\mathbf{Q}(\mathbf{x}, \mathbf{x}) \equiv \iint \delta n(\mathbf{r}) Q(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}') = \mathbf{x}^{\text{T}} \mathbf{Q} \mathbf{x} \quad (27)$$

where \mathbf{x} is a column vector with components x_i and \mathbf{Q} is the matrix representation of the operator Q in the given basis. In particular, we have from (24a)

$$\delta E_{\text{H}}[n^{\text{in}}] = \frac{1}{2} \mathbf{x}^{\text{T}} (\mathbf{K} - \mathbf{K} \mathbf{K}_0^{-1} \mathbf{K}) \mathbf{x}$$

where \mathbf{x} is the vector corresponding to $\delta n^{\text{in}}(\mathbf{r})$. We are interested in the extremal properties of this quadratic form.

What is required is the simultaneous diagonalisation of the \mathbf{K} and \mathbf{K}_0 matrices. This can be achieved by considering the generalised eigenvalue problem (Gantmacher 1959)

$$\mathbf{K}\mathbf{v} = \lambda\mathbf{K}_0\mathbf{v} \quad (28)$$

which according to (14), (15) and (17) is equivalent to

$$\boldsymbol{\varepsilon}^T\mathbf{v} = \lambda\mathbf{v} \quad (29)$$

i.e. λ is an eigenvalue of the dielectric matrix $\boldsymbol{\varepsilon} = \boldsymbol{\chi}^{-1}\boldsymbol{\chi}_0 = \mathbf{K}\mathbf{K}_0^{-1}$ (and its transpose). The characteristic equation defining the eigenvalues is

$$\det(\mathbf{K} - \lambda\mathbf{K}_0) = 0. \quad (30)$$

Since \mathbf{K}_0 is a real, symmetric matrix there exists an orthogonal transformation \mathbf{U}_0 ($\mathbf{U}_0^T\mathbf{U}_0 = \mathbf{I}$) such that

$$\mathbf{U}_0^T\mathbf{K}_0\mathbf{U}_0 = \mathbf{D}_0 \quad (31)$$

where \mathbf{D}_0 is a diagonal matrix whose diagonal elements μ_i are the eigenvalues of \mathbf{K}_0 . Since \mathbf{K}_0 is positive definite the eigenvalues satisfy $\mu_i > 0$. Defining the matrix $\mathbf{V}_0 = \mathbf{U}_0\mathbf{D}_0^{-1/2}$ ($\mathbf{V}_0^T\mathbf{V}_0 = \mathbf{D}_0^{-1}$), we then have

$$\mathbf{V}_0^T\mathbf{K}_0\mathbf{V}_0 = \mathbf{I}. \quad (32)$$

Since \mathbf{V}_0 is non-singular we may replace (30) by the equivalent equation

$$\det[\mathbf{V}_0^T(\mathbf{K} - \lambda\mathbf{K}_0)\mathbf{V}_0] = \det(\mathbf{V}_0^T\mathbf{K}\mathbf{V}_0 - \lambda\mathbf{I}) = 0 \quad (33)$$

which defines the eigenvalue problem for the matrix $\mathbf{V}_0^T\mathbf{K}\mathbf{V}_0$. This matrix is real and symmetric and may be diagonalised by an orthogonal matrix \mathbf{V} ($\mathbf{V}^T\mathbf{V} = \mathbf{I}$) such that

$$\mathbf{V}^T(\mathbf{V}_0^T\mathbf{K}\mathbf{V}_0)\mathbf{V} \equiv \mathbf{S}^T\mathbf{K}\mathbf{S} = \mathbf{D} \quad (34)$$

where the diagonal matrix \mathbf{D} has diagonal elements λ_i . We note that $\mathbf{V}_0^T\mathbf{K}\mathbf{V}_0$ is positive definite since $\mathbf{x}^T\mathbf{V}_0^T\mathbf{K}\mathbf{V}_0\mathbf{x} = \bar{\mathbf{x}}^T\mathbf{K}\bar{\mathbf{x}} > 0$, and therefore $\lambda_i > 0$. Using these results and defining $\mathbf{x} = \mathbf{S}\mathbf{y}$ we finally obtain

$$\delta E_H[n^{\text{in}}] = \frac{1}{2}\mathbf{x}^T(\mathbf{K} - \mathbf{K}\mathbf{K}_0^{-1}\mathbf{K})\mathbf{x} = \frac{1}{2}\mathbf{y}^T\mathbf{S}^T(\mathbf{K} - \mathbf{K}\mathbf{K}_0^{-1}\mathbf{K})\mathbf{S}\mathbf{y} = \frac{1}{2}\sum_i \lambda_i(1 - \lambda_i)y_i^2. \quad (35)$$

We next consider the quadratic form $\mathbf{x}^T\mathbf{C}\mathbf{x}$. We have

$$\mathbf{x}^T\mathbf{C}\mathbf{x} = \mathbf{x}^T(\mathbf{K} - \mathbf{K}_0)\mathbf{x} = \mathbf{y}^T\mathbf{S}^T(\mathbf{K} - \mathbf{K}_0)\mathbf{S}\mathbf{y} = \mathbf{y}^T(\mathbf{D} - \mathbf{I})\mathbf{y} = \sum_i (\lambda_i - 1)y_i^2. \quad (36)$$

From this we see that \mathbf{C} is positive definite if and only if the eigenvalues of the dielectric matrix, λ_i , are greater than one. We have thus established via equations (35) and (36) that the Harris energy functional has a local maximum at $n^{\text{in}} = n^{\text{sc}}$ if and only if the operator \mathbf{C} is positive definite. This operator is given by (10) which can be interpreted as an effective pair potential between two electrons at \mathbf{r} and \mathbf{r}' . The direct Coulomb interaction is clearly positive definite since

$$\iint \delta n(\mathbf{r}) \delta n(\mathbf{r}') |\mathbf{r} - \mathbf{r}'|^{-1}$$

is the electrostatic self-energy of the density distribution $\delta n(\mathbf{r})$. The second term is expected to be negative since the effective interaction between electrons is reduced by the formation of an exchange–correlation hole. Although we do not have a general proof

of the positive definiteness of \mathbf{C} , it is difficult to imagine that exchange and correlation should be so effective as to result in a tendency for the electrons to *antiscreen* a static external field. It should be emphasised that these comments pertain to the exact \mathbf{C} ; approximate exchange–correlation energy functionals may well generate a \mathbf{C} that is *not* positive definite. This in fact is the case for a uniform electronic system in the local density approximation.

A similar analysis of $\delta E_v[n^{\text{out}}]$ leads to the result

$$\delta E_v[n^{\text{out}}] = \frac{1}{2} \mathbf{x}^T \mathbf{C} \mathbf{K}_0^{-1} \mathbf{K} \mathbf{K}_0^{-1} \mathbf{C} \mathbf{x} = \frac{1}{2} \sum_i \lambda_i (\lambda_i - 1)^2 y_i^2 \quad (37)$$

which is clearly positive definite as it must be according to the variational principle. With (35) we can now investigate the relative rates at which $E_v[n^{\text{out}}]$ and $E_H[n^{\text{in}}]$ deviate from their extremal values. Adding (35) to (37) we find

$$E_v[n^{\text{out}}] - E_v[n^{\text{sc}}] + E_H[n^{\text{in}}] - E_v[n^{\text{sc}}] = \frac{1}{2} \sum_i \lambda_i (\lambda_i - 1) (\lambda_i - 2) y_i^2. \quad (38)$$

This result has a number of interesting implications. Even with $\lambda_i > 1$, the sum of deviations can be of either sign depending on the distribution of eigenvalues. If the eigenvalues are such that $1 < \lambda_i < 2$ then (38) is negative which implies that the variational energy estimate is better in absolute value than the Harris energy estimate. On the other hand, if the eigenvalue spectrum extends beyond two, one cannot state definitively which of the two functionals is superior; their relative merits depend not only on the physical system being considered but also on the specific form of the density variation. Nevertheless, if the density δn^{in} is such that the vector \mathbf{y} is dominated by components corresponding to large eigenvalues, equation (38) will be positive and the Harris energy functional will be closer to the exact answer than the variational estimate.

There is a close connection between the eigenvalue distribution and the question of convergence of the self-consistency procedure whereby an input density δn^{in} is used to generate an output density δn^{out} (Dederichs and Zeller 1983). A measure of the deviation from the stationary value is provided by the inner product $(\delta n^{\text{in}}, \delta n^{\text{in}}) = \mathbf{x}^T \mathbf{x}$. With $\mathbf{x} = \mathbf{D}_0^{1/2} \mathbf{S} \mathbf{y} = \mathbf{U}_0 \mathbf{V} \mathbf{y}$ we have

$$(\delta n^{\text{in}}, \delta n^{\text{in}}) = \mathbf{x}^T \mathbf{x} = \mathbf{y}^T \mathbf{y} = \sum_i y_i^2. \quad (39)$$

Similarly,

$$(\delta n^{\text{out}}, \delta n^{\text{out}}) = \mathbf{x}^T \mathbf{C} \mathbf{K}_0^{-2} \mathbf{C} \mathbf{x} = \sum_i (\lambda_i - 1)^2 y_i^2. \quad (40)$$

Thus if $0 < \lambda_i < 2$, $(\delta n^{\text{out}}, \delta n^{\text{out}}) < (\delta n^{\text{in}}, \delta n^{\text{in}})$ and the iterative procedure is absolutely convergent. An eigenvalue spectrum of this kind represents a condition of *weak* screening since it implies that ϵ is close to a unit matrix. Absolute convergence is thus conditional on weak screening and it is for this situation that the variational energy estimate is superior to that of the Harris functional. The *strong* screening limit is by definition a situation in which some of the eigenvalues exceed two and a straightforward iteration of the self-consistency procedure will in general diverge. In such a case the Harris energy functional would be expected to outperform the variational estimate. The examples considered by Polatoglou and Methfessel (1988) and by Finnis (1990) appear to belong to this category; this is not too surprising since a metallic system is one in which screening is certainly strong.

In summary, we have shown that the Harris energy functional has a local maximum at the true ground-state density provided the eigenvalues of the dielectric matrix are greater than unity. The latter property is normally expected on physical grounds; if and when it can be rigorously violated is not known at the present time.

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