Variational Principle for Eigenmodes of Reactivity in Conceptual Density Functional Theory

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ABSTRACT: In conceptual density functional theory, reactivity indexes as the Fukui function, the global hardness/softness, and hardness/softness kernels are fundamental linear responses extensively studied to predict the nucleophilic and electrophilic propensities of atoms in molecules. We demonstrate that the hardness/softness kernels of an isolated system can be expanded in eigenmodes, solutions of a variational principle. These modes are divided into two groups: the polarization modes and the charging modes. The eigenvectors of the polarization modes are orthogonal to the Fukui function and can be interpreted as densities induced at a constant chemical potential. The charging modes of an isolated system are associated with virtual charge transfers weighted by the Fukui function and obey an exact nontrivial sum rule. The exact relation between these charging eigenmodes and those of the polarizability kernel is established. The physical interpretation of the modes is discussed. Applications of the present findings to the Thomas–Fermi and von Weizacker kinetic energy functionals are presented. For a confined free quantum gas, described by the von Weizacker kinetic energy functional, we succeed to derive an approximate analytical solution for the Fukui function and for hardness/softness and polarizability kernels. Finally, we indicate how numerical calculations of the hardness kernel of a molecule could be performed from the Kohn–Sham orbitals.

INTRODUCTION

Conceptual density functional theory (CDFT) is one of the main theories aiming to fill the gap between raw ab initio data and an understanding of chemical reactivity. Initiated by the seminal work of Parr and Yang and collaborators, CDFT relates electronic structure numerical calculations to working empirical chemical concepts and provides new formal concepts to understand the propensities of atoms in molecules to react. CDFT has been developed since more than 30 years, and particularly active research groups who contribute to strengthening CDFT are the teams of Geerlings, Ayers, Chattaraj, Fuentealba, Cardenas, Nalewajski, among others. The literature on CDFT is huge, and the interested reader is invited to consult the following excellent reviews of CDFT. CDFT is mainly a linear response theory; the nonlinear chemical reactivity responses are introduced and formal relations are established between them, but they remain largely unexplored. It worth noting that nonlinear responses can be computed from the linear ones by quadrature. The central variables of CDFT are the responses of the molecular electron density to a variation of the electron number \( N \) or of the external potential \( v_{\text{ext}} \) of the molecule. The Fukui function and local and global softnesses are second derivatives of the energy and are extensively applied to describe the molecular reactivity. For an isolated system, these derivatives of the electronic energy relative to \( N \) are finite-difference derivatives, \( N \) being an integer. Extension of CDFT to a fractional number of electrons was developed in the Grand Canonical Ensemble. Alternatively, chemical reactivity of an isolated system can be described as responses to changes in the external potential of the reagents. The key quantity in this polarization approach of chemical reactivity is the polarizability density kernel, which measures the second-order change in the energy relative to a change in the external potential of the system. It was shown previously that global chemical hardness can be formulated as a screened interaction between the Fukui functions and is therefore closely related to the polarizability density kernel. Applications of the polarizability density kernel to reactivity were examined numerically mainly by the Geerlings group.

Here, we address the question of collective electronic modes for the polarizability density kernel and hardness kernel in the Born–Oppenheimer approximation at a constant electron number. These electronic modes were first introduced by Nalewajski and were examined by Mears and Kohn and Cohen and co-authors. We demonstrate that these modes are...
solutions of a variational principle. For the hardness kernel, the modes can be divided into polarization modes ( conserving the number of electrons) and charging modes (nonconserving the number of electrons). We demonstrate that the Fukui function is orthogonal to the eigenvectors of the polarization modes. Because of this property, the eigenvectors of the polarization modes are part of the eigenvectors of the polarizability density kernel. For isolated molecules, the noninteger number of electrons associated with each charging mode can be rigorously interpreted in terms of a virtual charge transfer induced by an external potential.

The paper is organized as follows. We first review briefly the linear response theory. Second, we examine the negativity of the linear response kernel, establish the variational principle for the polarizability and hardness kernels, and demonstrate the exact relation between the eigenmodes of the two kernels. Next, the physical interpretation of the electronic modes is discussed. Applications to Thomas–Fermi and von Weizacker kinetic energy functionals and numerical calculation of the hardness kernel are described. The paper ends with a brief conclusion.

## RESULTS AND DISCUSSION

### Linear Response Theory

We briefly summarize the linear response theory\(^1\) and introduce notation. One considers an isolated system. In the Born–Oppenheimer approximation, the system is described by an electrostatic Hamiltonian \(\hat{H}\) defined by the number of electrons \(N\) and the one-electron Coulomb potential due to the nuclei

\[
\hat{H} = \hat{F} + \sum_{i=1}^{N} v_{ext}(r_i)
\]  

(1)

where \(\hat{F}\) is independent of the nuclei positions

\[
\hat{F} = \sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1,j\neq i}^{N} \frac{\epsilon^2}{|r_i - r_j|}
\]

(2)

and

\[
v_{ext}(r) \equiv \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{Z_j}{|r_i - R_j|}
\]

(3)

In eq 3, \(M\) is the total number of nuclei, \(Z_j\) and \(R_j\) are respectively the nuclear charge and position of the \(j\)th atom.

Strictly speaking, a chemical reaction is a result of the displacement of the nuclei or in other words of a change in the external potential \(v_{ext}(r)\). For example, if the system is composed of two reagents \(A\) and \(B\), they are fully described by their respective external potential

\[
v_{ext}(r) = v_{ext, A}(r) + v_{ext, B}(r)
\]

(4)

and the reaction by a change in \(v_{ext}(r)\) at constant \(N\). It is worth emphasizing that \(\hat{F}\) cannot be separated in \(A\) and \(B\) as the electrons are indistinguishable.

According to the fundamental theorems of DFT, the lowest eigenvalue \(E_0\) of \(\hat{H}\), corresponding to the normalized ground-state wave function \(|\Psi_0\rangle\), is a functional \(E[\rho]\) of the electron density \(\rho(r)\).\(^{25–27}\) The so-called universal functional \(F[\rho]\) at the solution point is

\[
F[\rho_0] = \langle \Psi_0 | \hat{F} | \Psi_0 \rangle = E_0 - \int dr \rho_0(r)v_{ext}(r)
\]

(5)

where \(\rho_0(r)\) is the ground-state density. Several functionals \(F[\rho]\)\(^{25–27}\) can be constructed, which all obey the following relations

\[
E_{v_{ext}}[\rho_0(r)] = E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle
\]

(6)

and

\[
E_{v_{ext}}[\rho(r)] > E_0
\]

(7)

A variation of the external potential \(\Delta v_{ext}(r)\), as the displacement of an atom of reagent \(A\) toward reagent \(B\), for example, induces a variation in the electronic energy. For small \(\Delta v_{ext}(r)\), the energy can be expanded as a function of the perturbation potential. To the second-order, one has

\[
\delta E^{(2)}_{v_{ext}} = \int dr \left[ \frac{\delta E}{\Delta v_{ext}(r)} \right]_{0,N} \Delta v_{ext}(r) + \frac{1}{2} K[\Delta v_{ext}, \Delta v_{ext}]
\]

(8)

where we have introduced the bilinear functional

\[
K[\Delta v_{ext}, \Delta v_{ext}] \equiv \int dr \int dr' \left( \frac{\delta E}{\Delta v_{ext}(r)} \right)_{0,N} \Delta v_{ext}(r) \Delta v_{ext}(r')
\]

(9)

From eq 5, one deduces\(^1,2,5\)

\[
\left[ \frac{\delta E}{\Delta v_{ext}(r)} \right]_{0,N} = \rho_0(r)
\]

(10)

The second functional derivative in eq 9 is the polarizability density kernel \(\chi_{\chi}(r, r')\). It is related to the first-order density variation induced by the change in the external potential by the following relation

\[
\delta \rho(r) = \int dr' \chi_{\chi}(r, r') \Delta v_{ext}(r')
\]

(11)

Another important kernel, related to \(\chi_{\chi}\), is the so-called hardness kernel, which occurs when we apply a small change in the electronic density \(\delta \rho(r)\) at a constant external potential and a constant electron number \(N\).\(^1\) This density perturbation can be thought as the difference between the density computed from a trial wave function \(|\Psi\rangle\) and the ground-state wave function \(|\Psi_0\rangle\). To the second order, the change in energy due to this density perturbation is

\[
\delta E^{(2)}_{v_{ext}} = \int dr \left[ \frac{\delta E}{\delta \rho(r)} \right]_{0,N} \delta \rho(r) + \frac{1}{2} \left[ \delta \rho, \delta \rho \right]
\]

(12)

where we have introduced the bilinear functional

\[
\left[ \frac{\delta E}{\delta \rho(r)} \right]_{0,N} = C
\]

(13)

According to the variational principle (eqs 6 and 7), the first-order term in eq 12 vanishes and one finds for an \(N\)-representable density\(^1\)

\[
\left[ \frac{\delta E}{\delta \rho(r)} \right]_{0,N} = C
\]

(14)

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where $C$ is a constant.

The second functional derivative in eq 13 is the hardness kernel $h(r, r')$. As the density perturbation is at a constant external potential, one has

$$\left. \frac{\delta^2 E}{\delta \rho(r) \delta \rho(r')} \right|_{\delta \rho = 0} = \left. \frac{\delta^2 E}{\delta \rho(r) \delta \rho(r')} \right|_{\delta \rho = 0} = h(r, r')$$

For a stable ground-state, the hardness kernel has an inverse $h^{-1}(r, r')$, the softness kernel, defined by the following equation

$$\int dr' h^{-1}(r, r') h(r', r') = \delta(r - r')$$

The relation between the polarizability kernel and the hardness kernel was established by Berkowitz and Parr\textsuperscript{13}

$$\chi(r, r') = -h^{-1}(r, r') + \frac{1}{\eta} f(r) f(r')$$

where the Fukui function $f(r)$ and the global hardness $\eta$ are defined as integrals of the softness kernel\textsuperscript{1}

$$\int dr \int dr' h^{-1}(r, r') \equiv \frac{1}{\eta}$$

$$\eta \int dr' h^{-1}(r, r') = \eta \int dr' h^{-1}(r', r') \equiv f(r)$$

Finally, the global softness $S$ is the inverse of the global hardness $S \equiv 1/\eta$.

**Response $\chi_1$ is a Negative Kernel.** The hardness kernel $h(r, r')$ is evaluated at the ground-state density $\rho_0(r)$. It is a positive kernel, i.e., for any variation $\delta \rho(r) \neq 0$, one has

$$J[\delta \rho, \delta \rho] > 0$$

because of the variational principle (eqs 6, 7, and 12). As shown below, the bilinear functional $J$ is related to $K$ by

$$K[\Delta v_{ext}, \Delta v_{ext}] = -J[\delta \rho, \delta \rho]$$

Consequently, $\chi_1(r, r')$ is a negative kernel, i.e., for any variation $\Delta v_{ext}(r) \neq 0$, one finds

$$K[\Delta v_{ext}, \Delta v_{ext}] < 0$$

Result (22) can be also deduced from the one-electron orbital perturbation theory.\textsuperscript{6} One deduces that $\chi_1(r, r) < 0$ by inserting the Fermi pseudopotential, $\Delta v_{ext}(r) = \delta(r - r')$,\textsuperscript{28} in eq 22.

Equation 21 is demonstrated using eq 11 in eq 13

$$J[\delta \rho, \delta \rho] = \int dr \int dr' \Delta v_{ext}(r') \Delta v_{ext}(r'') D(r', r'') \chi_1(r', r'')$$

where

$$D(r', r'') = \int dr h(r', r') \chi_1(r', r'')$$

$$= -\delta(r' - r'') + f(r'')$$

in which the last line is found by using the Berkowitz–Parr relation (eq 17) in $D$. Using eq 24 in eq 23 and the electron number conservation

$$\int dr' \chi_1(r', r'') = 0$$

one finds eq 21.

**Variational Principle for Eigenmodes of $\chi_1$.** Because $\chi_1$ is a symmetric kernel, it can be expanded in its orthonormalized eigenmodes, solutions of the equation\textsuperscript{23}

$$\int dr' \chi_1(r, r') \Delta v_{ext}(r') = \lambda \Delta v_{ext}(r)$$

The largest eigenvalue, $\lambda_0$, is zero and corresponds to a trivial constant eigenvector. All other eigenvalues are negative, as $\chi_1$ is a negative kernel: $\lambda_0 > \lambda_1 > \lambda_2$. The eigenmodes of nonzero eigenvalues form a complete basis set and $\chi_1$ reads

$$\chi_1(r, r') = \sum_{n=1}^{\infty} \lambda \Delta v_{ext}(r) \Delta v_{ext}(r')$$

The physical unit of the eigenvalues is $1/(EV)$, where $E$ is the energy unit and $V$ is the volume unit, whereas the unit of the eigenvector is $1/\sqrt{V}$ (as the wave function). The eigenmodes can be deduced from a variational principle as follows. We consider external potentials which are square-integrable (this excludes the trivial constant potential)

$$\int dr \Delta v_{ext}^2(r) < \infty$$

and we search for the extremum of the following functional

$$K \left[ \frac{\Delta v_{ext}}{\sqrt{\Delta v_{ext}^2}}, \frac{\Delta v_{ext}}{\sqrt{\Delta v_{ext}^2}} \right] = \frac{\int dr \int dr' \Delta v_{ext}(r) \chi_1(r, r') \Delta v_{ext}(r')}{\int dr'' \Delta v_{ext}^2(r'')}$$

The functional derivative of $K$ (eq 29) is

$$\frac{\delta K}{\delta \Delta v_{ext}(r)} = \frac{2}{\int dr \Delta v_{ext}^2(r')} \left[ \int dr' \chi_1(r, r') \Delta v_{ext}(r') - \frac{\int dr' \Delta v_{ext}^2(r') \chi_1(r, r') \Delta v_{ext}(r')}{\int dr'' \Delta v_{ext}^2(r'')} \right]$$

One immediately find that the eigenmodes of the polarizability density kernel, eq 26, are solutions of the variational equation

$$\left. \frac{\delta K}{\delta \Delta v_{ext}(r)} \right|_{\Delta v_{ext} = \Delta v_{ext}} = 0$$

Mode 1 maximizes the bilinear functional $K$ for any potential perturbation, which is square-integrable (eq 28). Expanding any trial external perturbation $\Delta v_{ext}(r)$ (chosen normalized) in the $\chi_1$ eigenmodes

$$\Delta v_{ext}(r) = \sum_{n=1}^{\infty} c_n \Delta v_{ext}(r)$$

and using expression 32 in $K$ with eq 26, one finds
\[ K[\Delta \psi_{\text{ext}}(r), \Delta \psi_{\text{ext}}(r')] = \sum_{n=1}^{\infty} c_n^2 \lambda_n \]  

Because \( \lambda_1 > \lambda_n \) for \( n > 1 \), one demonstrates that the first mode maximizes the value of \( K \) for any nonconstant potential

\[ K[\Delta \psi_{\text{ext}}(r), \Delta \psi_{\text{ext}}(r')] < \lambda_1 \sum_{n=1}^{\infty} c_n^2, \]

\[ K[\Delta \psi_{\text{ext}}(r), \Delta \psi_{\text{ext}}(r')] < \lambda_1 \]

**Variational Principle for Eigenmodes of the Hardness Kernel.** As the hardness kernel is symmetric, it can be also expanded in its orthonormalized eigenmodes

\[ \psi(r, r') = \sum_{n=1}^{\infty} \beta_n \Delta \rho_n(r) \Delta \rho_n(r') \]  

solutions of the following equation

\[ \int \dd r' \psi(r, r') \Delta \rho_n(r') = \beta_n \Delta \rho_n(r) \]  

All eigenvalues are positive and the kernel is positive-define (the smallest eigenvalue, \( \beta_n \), is nonzero for a stable ground-state system, and we sort the values as \( \beta_1 < \beta_2 < \beta_3 \ldots \)). The physical unit of the eigenvalues is EV, where E is the energy unit and V is the volume unit, whereas the unit of the eigenvectors is \( 1/\sqrt{V} \) (as the wave function).

The softness kernel is

\[ h^{-1}(r, r') = \sum_{n=1}^{\infty} \frac{1}{\beta_n} \Delta \rho_n(r) \Delta \rho_n(r') \]  

Mode 1 contributes the most to the inverse kernel as \( \beta_1 < \beta_2 \) for \( n > 1 \).

The eigenmodes are solutions of a variational principle. We consider nonzero density variations that are square-integrable

\[ \int \dd r \Delta \rho_n^2(r) < \infty \]

Following the same lines as in the previous section, one defines the functional

\[ J = \left[ \frac{\Delta \rho}{\sqrt{\int \Delta \rho^2}}, \frac{\Delta \rho}{\sqrt{\int \Delta \rho^2}} \right] = \frac{\int \dd r \dd r' \Delta \rho(r) \psi(r, r') \Delta \rho(r')}{{\int \dd r' \Delta \rho^2(r')}}, \]

The first functional derivative is given by eq 30, with \( K \) replaced by \( f \), \( \Delta \lambda_n \) replaced by \( \Delta \rho_n \), which proves that the functional is extremum for the eigenmodes of the hardness kernel. Because \( f \) is positive, mode 1 minimizes the functional \( J \). Similarly, to the previous section, one considers a variation \( \Delta \rho_n \), which is square-integrable, and expands it in the eigenmodes \( \Delta \rho_n(r) \).

\[ |J[\Delta \rho(r), \Delta \rho_n(r')| > \beta_1 \sum_{n=1}^{\infty} d_n^2, \]

\[ |J[\Delta \rho(r), \Delta \rho_n(r')| > \beta_1 \]

with \( d_n = \int \dd r' \Delta \rho_n(r') \Delta \rho_n(r) \).

The eigenmodes of the hardness kernel were introduced for the first time by Nalewajski in the context of an empirical discrete model, the charge sensitivity analysis.\(^{22} \) To the best of our knowledge, the variational principle of the hardness kernel eigenmodes was not demonstrated before.

The integral of the eigenvector, i.e.

\[ \int \dd r \Delta \rho_n(r) = \Delta \rho_N \]  

permits to separate the modes as the polarization modes for which \( \Delta \rho_N = 0 \) and the others, we named charging modes, for which \( \Delta \rho_N \neq 0 \). \( \Delta \rho_N \) is interpreted as a virtual charge transfer as shown next. However, it is worth noting that \( \Delta \rho_N \) is not dimensionless, its unit is \( \sqrt{V} \), and this quantity is proportional to charge transfer.

The polarization modes have the nice property to be orthogonal to the Fukui function. Indeed, multiplying eq 19 by \( \Delta \rho_n \) and using eq 38, we find

\[ \int \dd r \Delta \rho_n(r)f(r) = \frac{\eta \Delta \rho_N}{\beta_n} \]

The term on the right-hand side is zero for the polarization modes. In a frozen-orbital approximation, the Fukui functions are approximated by the highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) densities, \( f(r) = |\psi_{\text{HOMO}}(r)|^2 \). The polarization eigenmodes of the hardness kernel are thus orthogonal to these frontier orbital densities in this approximation.

The Fukui function is built only from the charging modes. According to eqs 19 and 38

\[ f(r) = \sum_{\text{charging modes}} \frac{\eta \Delta \rho_N}{\beta_n} \Delta \rho_n(r) \]

Finally, the chemical hardness (eq 18) reads

\[ \frac{1}{\eta} = \sum_{\text{charging modes}} \frac{1}{\beta_n} \]

**Sum Rule for the Charging Modes.** Chattaraj et al. demonstrated a variational principle for the Fukui function by defining a functional based on the hardness kernel.\(^{29} \) In the present notation, the functional was \( \int [g(r)]^2 \Delta \rho_n(r) \) with \( g(r) \) an arbitrary normalized function. Minimizing \( \int \dd r g(r) \) with the constraint that \( \int \dd r g(r) = 1 \) leads to the following variational equation

\[ \int \dd r h(r, r') g(r') = \frac{\alpha}{2} \]

where \( \alpha \) is a Lagrange multiplier (a constant). The authors demonstrated that the solution of the variational equation (eq 46) is

\[ \int \dd r h(r, r') f(r') = \eta \]

in which \( f(r) \) and \( \eta \) are the Fukui function and the global hardness, respectively. Although eq 47 is sometimes used to defined the local hardness,\(^{30} \) a space-dependent property, the exact equation (eq 46) indicates that the local and global hardness are identical properties if the Fukui function and the hardness kernel are derived from the same energy functional in the ground state.

An interesting sum rule can be derived by inserting the eigenmode expansion of the Fukui function, eq 44, in the variational equation (eq 47). One finds
where we used the eigenmode equation of the hardness kernel \((36)\). Condition \((48)\) is a strong constraint for any hardness kernel model, as the sum must equal 1 for all points in space. It is worth noting that integration of both sides of eq 48 leads to a divergence on the right-hand side (excepted for a quantum gas confined in a finite volume).

**Exact Relation between the Modes of the Hardness Kernel \(h(r,r')\) and Those of the Polarizability Density Kernel \(\chi(r,r')\).** As shown by the Berkowitz–Parr relation, \(\chi_1\) is not the inverse of the hardness kernel because of the term depending on the Fukui function in eq \((17)\). Indeed, the polarizability response has a zero eigenvalue and the Berkowitz–Parr relation corresponds to the generalized inverse of \(\chi_1\). However, the eigenvectors of the polarization modes of the hardness kernel are also eigenvectors of \(\chi\), because of the orthogonality of these eigenvectors to the Fukui function. Moreover, one demonstrates the following exact relations that relate the eigenvalues and eigenvectors of \(\chi_1\) to those of the hardness kernel

\[
\lambda_n = -\frac{1}{\beta_n}
\]

\[
\Delta \nu_n(r) = \Delta \rho_n(r) - f(r)\Delta_nN
\]

Indeed, using eq 49 in expansion \((27)\), one finds

\[
\chi(r, r') = -\sum_{n=1}^{\infty} \frac{1}{\beta_n} \Delta \rho_n(r) \Delta \rho_n(r') + f(r) \left[ -\sum_{n=1}^{\infty} \frac{1}{\beta_n} \Delta \rho_n(r') \Delta_nN \right] + f(r') \left[ -\sum_{n=1}^{\infty} \frac{1}{\beta_n} \Delta \rho_n(r) \Delta_nN \right] - f(r)f(r') \left[ -\sum_{n=1}^{\infty} \frac{1}{\beta_n} \left(\Delta_nN\right)^2 \right]
\]

The first term on the right-hand side of eq 50 is minus the softness kernel (see eq \((38)\)). The expressions in brackets in the second and third terms on the right-hand side of the equation are, respectively, \(f(r)\) and \(f(r')\) (see eq \((44)\)). Finally, the last term in brackets is \(1/\eta\) (see eq \((45)\)). Therefore, the sum of all of these terms is exactly the Berkowitz–Parr relation (eq \((17)\)). Equation 49 is fundamental as it shows that each mode of the polarizability density kernel is built from a polarization or a charging mode of the hardness kernel.

It is interesting to compare the eigenmode expansion of the polarizability kernel with its expansion in terms of quantities related to the exact wave functions of the many-body Hamiltonian \((eq 1)\). Indeed, the polarizability response of an electron gas of \(N\)-interacting Fermions is given exactly by

\[
\chi(r, r') = -\sum_{n=1}^{\infty} \frac{a_{00}(r) a_{00}(r')}{E_{n0}}
\]

with the following notation

\[
a_{00}(r) = \sqrt{2} \int \Psi_0(r, r_2, ..., r_N) \Psi_0(r, r_2, ..., r_N) dr_2 ... dr_N,
\]

\[
a_{00}^*(r') = \sqrt{2} \int \Psi_0^*(r', r_2, ..., r_N) \Psi_0^*(r', r_2, ..., r_N) dr_2 ... dr_N
\]

\[
E_{00} = E_a - E_0
\]

where \(E_a\) and \(\Psi_i\) \((0 \leq i < \infty)\) are the eigenvalues and normalized eigenfunctions of the \(N\)-electron Hamiltonian \((eq 1)\). It is thus tempting to interpret the eigenvalues \(\beta_n\) as excitation energies proportional to \(E_{00}\). However, the \(\Delta \nu_n(r)\) cannot be simply proportional to \(a_{00}(r)\) as the later are not eigenvectors of \(\chi\).

**Physical Interpretation of the Charging and Polarization Modes.** The physical meaning of the modes of the hardness kernel can be understood as follows. Let us consider an external potential perturbation in the direction of one of the eigenvectors of the hardness kernel. More precisely, we choose

\[
\Delta \nu_{n=0}(r) = -\beta_n \frac{\Delta \rho_n(r)}{\sqrt{\Omega}}
\]

where \(\Omega\) is an arbitrary volume to ensure the correct physical dimension of \(\Delta \nu_{n=0}\). The volume \(\Omega\) can be arbitrarily chosen equal to 1 in the following. The density induced by this potential is of the first order according to eqs 11, 17, and 38

\[
\delta \rho(r) = \delta \rho_{n=0}(r) - f(r)\Delta N
\]

We have shown that for any external potential applied to an isolated system \(19\)

\[
\delta \rho(r) = \delta \rho_{n=0}(r) - f(r)\Delta N
\]

where \(\Delta N\) is interpreted as a virtual charge transfer. The virtual charge transfer corresponds to the charge arising from all of the regions of the molecule, in proportion to the Fukui function, to build \(\delta \rho_{n=0}(r)\), we named as polarization charge.\(19\) The polarization charge is the density induced at a constant chemical potential, i.e., when the molecule is in contact with an infinite reservoir of electrons. The spatial variation of the polarization charge depends on the external potential (the first term in eq 56), whereas the spatial variation of the virtual charge transfer depends only on the Fukui function (the second term in eq 56).

To illustrate eq 56, let us consider a molecule in contact with a metal surface (an infinite reservoir of electrons) and an external perturbing potential generated by a point charge outside the molecular surface. The density induced by the external potential will be localized in the vicinity of the perturbating point charge, and it will decrease with the distance from this point perturbation. The integration of this density induced by the external perturbation represents the number of electrons, \(\Delta N\), transferred from the reservoir to the molecule to build the polarization charge \(\delta \rho_{n=0}(r)\). For an isolated molecule, the reservoir is the molecule itself and the \(\Delta N\) electrons arise from all of the regions of the molecule with a weight equal to \(-f(r)\Delta N\). Therefore, for an isolated molecule, the number of electrons \(\Delta N\) can be interpreted as a virtual charge transfer and can be fractional, it is a continuous variable. It is worth noting that the virtual charge transfer can be zero by symmetry. For example, two point charges of opposite signs may induce a dipolar electronic density, \(\delta \rho_{n=0}(r)\), which integrates to zero.\(19\) One concludes that the polarization and charging eigenvectors \(\Delta \nu_n(r)\) of the hardness kernel and their integral \(\Delta \nu N\), to an arbitrary factor \(1/\sqrt{\Omega}\), can be interpreted as elementary
densities induced at constant chemical potential and as virtual charge transfers, respectively. Note that the virtual charge transfer is exactly one electron by construction for the perturbation \( \Delta \nu_{\text{ext}}(r) = -\beta_k \delta(r) / \Delta_0 N \), where \( n \) is for a charging mode.

**Application to Model Functionals.** The eigenmodes of the hardness and polarizability kernels remain to be explored. In the hope to gain some insight, it is interesting to examine the eigenvectors of the hardness kernel of explicit models of the energy functional.\(^{31-35}\) However, the simplest local-density approximation (LDA) functional models fail. To give an example, let us consider the Thomas–Fermi functional of the kinetic energy functional:\(^{32}\)

\[
T_{\text{TF}} = C_F \int dr \rho^{5/3}(r)
\]  

(57)

where \( C_F = 3\hbar^2/10m(3\pi^2)^{2/3} \). The second functional derivative of \( T_{\text{TF}} \) in the ground state is \( h_{\text{TF}}(r, r') = 10C_F \delta(r - r') / 9 \rho_0^{1/3}(r) \). Using eq 58 in the eigenvalue equation (eq 37), one finds

\[
10C_F / 9\rho_0^{1/3}(r) \equiv \beta_n
\]  

(59)

which has no solution because the electronic density \( \rho_0 \) is not constant in an actual molecule. One may approximate \( \rho_0(r) \) by its average value, \( \langle \rho_0(r) \rangle \equiv \bar{\rho}_0 \). One observes that all eigenvalues are degenerate, \( \beta_n = \eta_{\text{TF}} \Omega \), where \( \eta_{\text{TF}} = 10C_F/9\Omega\rho_0^{1/3} \) is the TF global hardness (see the definition (18)) and \( \Omega \) is the volume confining the electron gas. In the TF model, the eigenvectors remain arbitrary. No useful information can be actually extracted from the TF model. On the contrary to the Thomas–Fermi functional, we conjecture that the hardness kernel of the von Weizacker kinetic energy model obeys the exact sum rule (48).

**Fermi Functional of the Ground State.** To illustrate the properties of the polarization density kernel for the von Weizacker functional in the present approximation, we have represented the diagonal elements of \( \chi_i(x, x') \) as well as those of \( \chi_i^0(x, x) = \chi_i(x, x) \) (the response at a constant chemical potential) in Figure 1 for \( L = 1 \). The diagonal elements of the polarization density kernel represent the local deformation of the density due to a repulsive localized external potential (the Fermi pseudopotential), i.e., \( \Delta \nu_{\text{ext}}(x) = A\delta(x - x') \). The response \( \chi_i^0 \) represents the contribution of the polarization modes to \( \chi_i \). In absolute values, the response \( \chi_i^0(x, x) \) is maximum exactly at \( x =
L/4 and x = 3L/4. The contribution of the charging modes reduces the response due to the contribution of the Fukui function. The contribution of the charging modes is maximum at the center of the box and decreases to the ends. The maxima (in absolute values) of \( \chi_n(x, x) \) are located at \( x = 0.23L \) and \( x = 0.77L \) compared to \( x = L/4 \) and \( x = 3L/4 \) at a constant chemical potential. Although the density is uniform, the wave character of the eigenmodes produces a very inhomogeneous response. As the polarization energy due to the localized perturbation illustrated in Figure 1 is proportional to \( \Delta E = A \rho_0 + \frac{\Delta^2 \chi}{2} (x, x) \), a moving particle with this repulsive potential needs to cross a barrier of the confined box to move from the local minimum on the left (located at about L/4) to the right (located at about 3L/4). This example shows the importance of the boundary conditions and the nonlocal character of \( \chi_n \), which depends on the nonlocality of the kinetic energy functional.

To illustrate the influence of the boundary conditions, we have also computed the polarization response for periodic boundary conditions (PBC), i.e., \( k_n = 2n\pi/L, n = 1, 2, \ldots \). Because the system is infinite, the global hardness should be zero because the chemical potential cannot change for a macroscopic system. This is a spectacular consequence of a large size that should apply approximately also to large macromolecules. For a periodic box, all of the modes of the density polarization kernel are polarization modes because all of the eigenvectors integrate to zero

\[
\Delta N_n(PBC) = \frac{2}{L} \int_0^L dx \sin \left( \frac{2n\pi}{L} x \right) = 0
\]  

Consequently, from eqs 45 and 44, the hardness and the Fukui function are zero. For PBC, the eigenvectors and eigenvalues of the density polarization kernel \( \chi_1 \) are easily found

\[
\Delta \chi_n(x)(PBC) = \frac{2}{L} \sin \left( \frac{2n\pi}{L} x \right)
\]  

(71)

\[
\beta_n(PBC) = 4\beta_n
\]  

(72)

Function \( \chi_1(x, x)(PBC) \) is compared to the polarizability density responses for confined boundary conditions in Figure 1. Because of the change of the boundary conditions, the response has four maxima and is exactly zero at the box center as at the box ends. Also, the response is strongly reduced by factor 4.

Finally, for the quantum gas confined in the box, it is interesting to compare the Fukui function with the contribution of the first and second charging modes to the sum over states in eq 68. The Fukui function \( f(x) \) is maximum at \( x = L/2 \), where it is exactly equal to 3/2L (see the Appendix and Figure 2). The contribution of the first charging mode, which is also the mode that minimizes the hardness functional \( f \) (see eq 40), is very close to the Fukui function, as shown in Figure 2. Indeed, the contribution of the polarization modes to the Fukui function decreases as \( 1/n^3 \).

It is worth noting that the von Weizacker kinetic energy functional is exact for a one-electron system and for an arbitrary number of noninteracting bosons. The zero chemical hardness found for a periodic system in the confined quantum gas with PBC does not mean of course that the gap (the difference between the ionization potential and the electronic affinity) is null for an extended electron gas that obeys the Pauli principle. Unfortunately, the formulation of the Pauli principle as an explicit functional is still an open problem. When specific solutions can be found, the functional is highly nonlocal. Adding the Thomas–Fermi functional to a weighted von Weizacker functional takes into account approximately the Pauli principle. For a molecular system, it is worth noting also that eq 61 can be extended by including the Thomas–Fermi model hardness kernel and the contributions of the second functional derivative of the Coulomb repulsion, \( h_C(r - r') = \frac{1}{|r - r'|} \), and those of the exchange-correlation functionals. In this case, the variational equation is an integrodifferential equation similar to the first-order density perturbation equation of the Thomas–Fermi–Dirac–von Weizacker energy functional (see equations (77) and (78) in ref 10). Alternatively to model functionals, more realistic calculations of hardness eigenmodes could be performed using the Kohn–Sham theory as explained in the next section.

**Toward Numerical Calculations of the Eigenmodes of the Hardness Kernel.** Apart from the explicit calculations of the eigenmodes for model functionals, the eigenmodes of the hardness kernel could be computed from the Kohn–Sham orbitals by following the method proposed by the Geerlings group for the numerical computation of the polarizability density kernel. The main idea developed by the authors is to apply a set of perturbations to the system and to expand the response in a finite basis set. It is worth noting that this method allows a straightforward study of the polarization modes by diagonalizing the kernel \( \chi_1 \) computed numerically in ref 6.
For the numerical calculation of the hardness kernel, we can follow exactly similar lines than those in ref 6. Instead of applying perturbative potentials, we may apply a set of perturbative densities $\delta \rho(i, r)$ to the system at constant external potential $\nu_{ext}(r)$. The first-order variation of the energy is

$$E(\rho_0 + \delta \rho) - E(\rho_0) = \int \text{d}r \left[ \frac{\delta E}{\delta \rho(r)} \right]_{\partial \nu_{ext}} \delta \rho(r) = 0$$

(73)

The last equality is due to the variational principle of DFT. The second-order variation of the energy is

$$E(\rho_0 + \delta \rho(i)) = -2E(\rho_0) + E(\rho_0 - \delta \rho(i))$$

$$= \int \text{d}r \int \text{d}r' \left[ \frac{\delta E}{\delta \rho(r) \delta \rho(r')} \right]_{\partial \nu_{ext}} \delta \rho(i, r) \delta \rho(i, r')$$

(74)

Expanding the second derivative in a basis set $\{ \theta_j(r) \}$ with $j = 1$ to $K$, one has

$$\left[ \frac{\delta E}{\delta \rho(r) \delta \rho(r')} \right]_{\partial \nu_{ext}} = h(r, r') = \sum_{k=1}^{K} \sum_{l=1}^{K} c_{kl} \theta_k(r) \theta_l(r')$$

(75)

where the coefficients $c_{kl}$ are found by solving the linear matrix equation

$$d = Gc$$

(76)

where $G$ is now a $P \times K^2$ matrix (with $P$ being the number of perturbations)$^6$

$$G_{ik(k-1)K+1} = \int \text{d}r \delta \rho_i(r) \theta_k(r) \int \text{d}r' \theta_l(r') \delta \rho_l(r')$$

(77)

and following ref 6, $c$ is a $K^2$-dimensional column matrix with elements $c_{ik(k-1)K+1} = c_{kl}$. The system can be solved using the generalized inverse $G^2$

$$GG^2G = G$$

(78)

The main question is to build a set of perturbations $\delta \rho(i, r)$ and $-\delta \rho(i, r)$ to compute the energy from the corresponding modified set of Kohn–Sham orbitals. For example, we may replace a Kohn–Sham orbital $\phi(r)$ by $\phi_1(r)g_1(r)$, where $g_1(r)$ is a model function. Assuming the functions $\phi_i(r)$ and $g_i(r)$ real for simplicity, the resulting density variation is

$$\delta \rho(i, r) = (g_i(r)^2 - 1)\phi_i(r)^2$$

(79)

The opposite variation of density $-\delta \rho(i, r)$ can be built by replacing the Kohn–Sham orbital $\phi_i(r)$ with $\phi_i(\sqrt{2 - g_i(r)^2})$ with $g_i(r) \leq 2$. To conserve the electron number, one may impose

$$\int \text{d}r g_i(r)^2 \phi_i(r)^2 = 1$$

(80)

\section{CONCLUSIONS}

In conclusion, we derived variational principles for the eigenmodes for the linear polarizability and hardness kernels. The polarization and charging modes for model functionals remain unexplored. The computation of these modes from explicit energy density functionals and for the Kohn–Sham density functional theory was discussed. For the first time, analytical expressions for the Fukui function of a quantum gas were derived using the explicit von Weizacker kinetic energy functional. We hope that the present formal work will stimulate numerical investigations and applications to chemical reactivity in the future.

\section{APPENDIX}

Mathematical useful formulas are given here for completeness. The proof of orthogonality between the polarization eigenmodes and the Fukui function of a uniform quantum gas involves the following integral

$$\int_0^\pi \sin^{-1}(x) \sin(ax) \text{d}x = \frac{\pi \sin(\pi a/2)}{2^{\nu-1} B\left(\frac{\nu+s+1}{2}, \frac{\nu-s+1}{2}\right)}$$

(81)

with $\nu = 3$ and $B$ being the beta function (see Section 3.63 in ref 38). Derivation of the expression of the global hardness (eq 67) involves the sum of the inverse fourth power of odd integer numbers

$$s \equiv \sum_{j=1}^{\infty} \frac{1}{(2j-1)^4}$$

(82)

The value of $s$ can be found using the Riemann $\zeta$ function

$$\zeta(4) \equiv \sum_{j=1}^{\infty} \frac{1}{j^4} = \sum_{j=1}^{\infty} \frac{1}{(2j)^4} + s$$

$$= \frac{\zeta(4)}{16} + s$$

(83,84)

one deduces

$$s = \frac{15 \zeta(4)}{16} = \frac{\pi^4}{96}$$

(85)

because $\zeta(4) = \frac{\pi^4}{90}$ (see Section 0-23 in ref 38).

The maximum value of the Fukui function is 3/2 because (see Section 0-23 in ref 38)

$$\sum_{j=1}^{\infty} (-1)^{k+1}(2j-1)^3 = \frac{\pi^3}{32}$$

(86)

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Notes

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