Simultaneous Relaxation of Nuclear Geometries and Electric Charge Densities in Electronic Structure Theories

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A simple formalism is presented, within the density-functional approach, which constitutes a powerful scheme for *directly* calculating the ground-state energy of systems with arbitrarily located nuclei and their accompanying electrons. The method permits *simultaneous* relaxation of both the atomic geometries and the electronic charge densities of polyatomic systems towards equilibrium. It circumvents the far less efficient indirect (*consecutive*) approach in which the equilibrium geometry is determined after calculation of energies on the Born-Oppenheimer surface.

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Most calculations of the electronic structure of polyatomic systems assume the equilibrium positions of the nuclei to be known. These are taken, when available, from various diffraction and scattering data. A lack of, or significant uncertainties in, such data often impedes electronic structure calculations on complex but interesting systems such as polymers, amorphous materials, relaxed surfaces, interfaces and defects, chemisorption systems, reaction intermediates, grain boundaries, etc. Such systems could be investigated if one could calculate simultaneously the equilibrium positions of the nuclei $\{\vec{R}_\alpha\}$ and the self-consistent electronic charge density $\rho(\vec{r};\{\vec{R}_\alpha\})$ of many-atom systems under the influence of prescribed external potentials $V_{\rm ext}(\vec{r})$. This can be achieved in principle by finding the stationary points of the total energy $E[\{\vec{R}_\alpha\},\rho(\vec{r})]$ of the electrons and the nuclei in a fixed $V_{\rm ext}$. Recently,[1] it has become practical to compute the equilibrium structure of simple crystalline solids by calculations of $E[\rho(\vec{r})]$ for a few selected sets of $\{\vec{R}_\alpha\}$ values and locating the minimum of E. This constitutes an *indirect* procedure for finding the equilibrium geometry: First find a self-consistent $\rho(\vec{r})$ at a fixed trial configuration $\{\vec{R}_\alpha\}$ and then change $\{\vec{R}_\alpha\}$ to reduce E, etc. These calculations treat the relaxation of the charge density and nuclear positions *consecutively,* changing only one or the other at each iteration. This approach hence involves the mapping out of a section of the Born-Oppenheimer (BO) surface and the search for the energy minimum on this surface. Except for special cases where the approximate geometry is known at the outset, this process is grossly inefficient because it requires considerable effort to refine one's knowledge of the details of the electronic charge distribution $\rho(\vec{r})$ for atomic geometries $\{\vec{R}_\alpha\}$ that may be far from equilibrium or even physically irrelevant. This limits the method to systems with a small number of configurational degrees of freedom.[1] In this Letter a simple formalism[2] is presented, within the density-functional approach,[3] in which the geometries and charge densities of general polyatomic systems can be varied *simultaneously,* allowing *direct* calculations of the equilibrium without intermediate knowledge of the BO surface. This provides a powerful and efficient method for the calculation of the ground-state properties of systems with arbitrarily located nuclei, and their accompanying electrons.

This is made possible by the following physical ideas. First, we conceive the Hohenberg-Kohn[3] total-energy functional to include the nuclear coordinates $\vec{R}_\alpha$ as variational parameters in addition to the charge density $\rho(\vec{r})$. Then, rather than describing the departure of the system from equilibrium in both $\{\vec{R}_\alpha\}$ and $\rho(\vec{r})$ by the scalar quantity[1] $E[\vec{R},\rho]-E_{\rm min}[\vec{R}^*,\vec{\rho}^*]$, we represent it in terms of kinematic vector restoring forces $\vec{F}_\alpha$ and $\vec{F}_\rho$ acting on the nuclei and charge densities, respectively. Since forces have a larger informational content (directions) than energies, they will better specify the variations needed to lower $E[\vec{R},\rho]$. Second, since the standard approach for calculating forces through the Hellmann-Feynman theorem[4] is of little practical use[5] unless one knows the exact self-consistent density $\rho(\vec{r})$ (the errors in the Hellman-Feynman forces are first order in the errors in ρ, whereas the errors in E are only second order), we will develop a formalism for generalized forces, correct to *second order* in $\rho(\vec{r})$, which can be used as a guide toward equilibrium even for non-self-consistent densities. Third, we will show that the conditions for the combined equilibrium, $\vec{F}_\alpha = 0$ and $\vec{F}_\rho = 0$, can be treated as a set of *simultaneous* nonlinear equations in which the most computionally unwieldy terms are eliminated by a transformation. In this representation it becomes possible to treat all $\{\vec{R}_\alpha\}$ and $\rho(\vec{r})$ as mathematically equivalent variational parameters, on an equal footing. We are considering the energy as a hypersurface defined for stationary as well as nonstationary configurations of $\{\vec{R}\}$ and $\rho(\vec{r})$ [the Born-Oppenheimer surface is its subsurface containing the locus of all points stationary with respect to $\rho(\vec{r})$ alone]. Whereas the traditional approach[1] restricts one to configurations on the BO surface, in the present philosophy one expects to travel through fewer sample points on the hypersurface by making simultaneous variations in both $\{\vec{R}\}$ and $\rho(\vec{r})$. Fourth, we will note that the equations for equilibrium, $\vec{F}_\alpha = 0$ and $\vec{F}_\rho = 0$, are amenable to efficient solution using recent ideas from optimization theory. Our formalism provides considerable insight into the reasons for the failure and success of contemporary methods for calculating equilibrium geometries of solids and molecules.

The density force.—Hohenberg, Kohn, and Sham[3] (HKS) have shown that the ground-state charge density ρ and the total energy E of electrons moving in an external potential $V_{\text{ext}}(\vec{r})$ can be obtained from

$$E = T + E_{ee} + E_{xc} + \int V_{\text{ext}}(\vec{r})\rho(\vec{r})\, d^3r + E_N, \tag{1}$$

by finding the density ρ^* that minimizes E. Here, T is the kinetic energy of noninteracting particles of density ρ, E_{ee} is the electrostatic energy of ρ, E_{xc} is the exchange-correlation energy, and E_N is the internuclear repulsion energy. For polyatomic systems we interpret V_{ext} as arising from a superposition over nuclear positions $\vec{R}_\alpha$ of site potentials $v_\alpha(\vec{r} - \vec{R}_\alpha)$ (e.g., $-Z_\alpha/r$, where Z_α is the atomic number). To find the minimizing density ρ^* one considers the single-particle equation for fictitious noninteracting electrons,

$$\{-\tfrac{1}{2}\nabla^2 + U(\vec{r})\}\psi_j(\vec{r}) = \epsilon_j \psi_j(\vec{r}), \tag{2}$$

and its corresponding charge density

$$\rho(\vec{r}) = \textstyle\sum_j N_j |\psi_j(\vec{r})|^2, \tag{3}$$

where N_j are occupation numbers and $U(\vec{r})$ is an ordinary function of $\vec{r}$. For any physical density ρ we assume[6] that there exists a potential U that can produce through Eqs. (2) and (3) a density for noninteracting particles that is identical to the ground-state physical density. The problem of finding the energy-minimizing density ρ^* is therefore transformed into the problem of varying the parameters $\{\mu_p\}$ which define a parametric $U(\vec{r}; \{\mu_p\})$, in search of $E[\rho^*(U)] = \min$. The density-generating potential U has no physical meaning except that it produces ρ, to be used together with the physical potential V_{ext} in minimizing E in Eq. (1).

HKS have chosen a particular interpretation for U based on a wave-function gradient principle, $\partial E/\partial\psi = 0$, and on $T = \sum_j N_j \langle \psi_j | -\frac{1}{2}\nabla^2 | \psi_j \rangle$. This yields for Eq. (2) a potential $V_{\text{KS}}[\rho] = V_{ee} + V_{xc} + V_{\text{ext}}$, where $V_{ee}[\rho]$ and $V_{xc}[\rho]$ are related differentially to E_{ee} and E_{xc}, respectively.[3] We will treat U rather than ρ or ψ as the fundamental independent variable; the three quantities bear a correspondence by Theophilou's theorem.[6] When we employ the potential-gradient principle[7] $\partial E/\partial\vec{\mu} = 0$, the stationarity condition (mathematically equivalent to HKS self-consistency) is that $\partial E/\partial\vec{\mu}$ equal

$$2\,\mathrm{Re} \sum_j \sum_{j'} N_j \frac{\langle j | V_{\text{KS}} - U | j' \rangle \langle j' | \partial U/\partial\mu_p | j \rangle}{\epsilon_j - \epsilon_{j'}} = 0. \tag{4}$$

The condition is obviously satisfied when $V_{\text{KS}}[\rho^*] - U(\vec{r}, \vec{\mu}_p) = 0$ (collecting all μ's into a vector $\vec{\mu}_p$), implying that at the solution $\vec{\mu}_p{}^*$, V_{KS} can be expressed in the same analytical form as U. We assume that this is also true for some domain around $\vec{\mu}_p{}^*$, i.e., there exists a set $\vec{\nu}_q$ such that $V_{\text{KS}}[\vec{r}, \rho(\vec{\mu}_p)] = U[\vec{r}, \vec{\nu}_q(\vec{\mu}_p)]$, where $\vec{\nu}$ is obtained deterministically from $\vec{\mu}$ [e.g., by calculating the components of $\vec{\nu}$ so that $U(\vec{r}, \vec{\nu}) = V_{\text{KS}}(\vec{r}, \vec{\rho})$]. The condition $\vec{\nu}_q(\vec{\mu}_p{}^*) = \vec{\mu}_q{}^*$ for stationary E can be obtained from the roots of the vector function[8] (i.e., by solving a simultaneous set of nonlinear equations)

$$\vec{F}_\rho(\vec{\mu}^*) = \vec{\nu}(\vec{\mu}^*) - \vec{\mu}^* = 0, \tag{5}$$

where $\vec{F}_\rho$ is the "density force" which can be used to aid in finding the minimizing density $\rho^*[U(\mu^*)]$. Practical and accurate methods for calculating $\vec{\nu}(\vec{\mu})$ for arbitrary solids have been described previously.[7]

The force on nuclei.—The force $\vec{F}_\alpha$ acting on each nucleus at $\vec{R}_\alpha$ can be derived by taking analytic gradients $\nabla_{\vec{R}_\alpha} E$. The Hellmann-Feynman (HF) theorem[4] states that the exact force $\vec{F}_\alpha$ equals the negative gradient of the classical electrostatic potential set by all positively charged nuclei and by the quantum mechanical electronic density ρ, i.e.,

$$\vec{F}_\alpha{}^{\mathrm{HF}} = -\frac{\partial E}{\partial \vec{R}_\alpha} = \sum_{\alpha' \neq \alpha} \frac{Z_\alpha Z_{\alpha'}(\vec{R}_\alpha - \vec{R}_{\alpha'})}{|\vec{R}_\alpha - \vec{R}_{\alpha'}|^3} + \int \frac{dv_\alpha}{d\vec{r}'}\bigg|_{\vec{r}' = \vec{r} - \vec{R}_\alpha} \rho(\vec{r})\, d^3r. \tag{6}$$

Unfortunately, this puristic theorem is of little practical help. It holds only for ρ calculated from the exact ψ (or certain types of fully optimized ψ) and when ρ is exactly self-consistent. In practice, the linear combinations over finite basis sets which are used to expand ψ do not provide exact eigenstates to $\hat{H} = -\frac{1}{2}\nabla^2 + U$. Furthermore, general points on the $\vec{R}$-ρ hypersurface do not correspond to self-consistent ρ. This often leads to huge errors in the calculated forces, rendering $\vec{F}_\alpha{}^{\mathrm{HF}}$ useless, even if the basis set produces acceptably small errors[5] in E. Fortunately, however, one can derive two *analytic* corrections to the HF force, within the same approximations used to calculate E. They represent corrections due to the use of an incomplete basis set (IBS) and non-self-consistent (NSC) charge densities. The combined force is identical to that computed from the negative of the numerical pointwise total energy derivatives, except that it is analytic and that a single force calculation is equivalent to $3N-6$ total-energy calculations for an N-atom system. The IBS and NSC forces will (i) cancel the first-order error in $\vec{F}_\alpha{}^{\mathrm{HF}}$, (ii) permit a proof of the limits in which self-consistent wave functions obey the HF theorem, and (iii) provide strategies for constructing basis functions that best satisfy the HF theorem.

We derive the generalized nuclear force from Eqs. (1)–(3) by taking the *total* derivative of the energy (including all implicit dependences) rather than the *partial* derivatives which give Eq. (6). We use the HKS definition of T, and the commonly encountered situation where the linear combinations of the basis set $\chi(\vec{r})$ diagonalize the finite matrix of $\hat{H}$ [i.e., $\psi_j(\vec{r}) = \sum_i a_{ji}\chi_i(\vec{r})$ satisfies the single-particle equation (2) within the subspace[9] χ_i]. We avoid the stronger, unpractical condition that ψ be an exact eigenstate ($\hat{H}\psi = \epsilon\psi$) of the operator $\hat{H}$. The general basis set $\{\chi\}$ may contain both functions that depend on the nuclear positions (e.g., linear combination of atomic orbitals), as well as originless orbitals (e.g., plane waves). We calculate $dT/d\vec{R}_\alpha$ by defining T from Eq. (2), $d\epsilon_j/d\vec{R}_\alpha$ by differentiating the normalized expectation value of $\hat{H}$, assuming that the only part of $\hat{H}$ that depends on $\vec{R}_\alpha$ is $U(\vec{r})$, and $d\psi_j/d\vec{R}_\alpha$ from the expansion of ψ_j in χ. The final results can be written in a very compact and simple form as

$$\vec{F}_\alpha{}^{\mathrm{IBS}} = -2\textstyle\sum_j N_j \operatorname{Re}\{\sum_i a_{ji}{}^*\langle d\chi_j/d\vec{R}_\alpha|\hat{H} - \epsilon_j|\psi_j\rangle\}, \tag{7a}$$

and

$$\vec{F}_\alpha{}^{\mathrm{NSC}} = -\int (d\rho/d\vec{R}_\alpha)[V_{\mathrm{KS}} - U]\,d^3r. \tag{7b}$$

The bracketed term in Eq. (7b) is the difference between the physical potential and the effective potential; it hence vanishes if self-consistency is attained.[7] The equilibrium condition for the total force on the nuclei $-dE/d\vec{R}_\alpha$ is

$$\vec{F}_\alpha = \vec{F}_\alpha{}^{\mathrm{HF}} + \vec{F}_\alpha{}^{\mathrm{IBS}} + \vec{F}_\alpha{}^{\mathrm{NSC}} = 0. \tag{8}$$

A similar (but more complex) expression has been derived for $\vec{F}_\alpha{}^{\mathrm{IBS}}$ in the context of the molecular Hartree-Fock method by Pulay.[10] $\vec{F}_\alpha{}^{\mathrm{IBS}}$ in (7a) cancels the first-order basis set error in $\vec{F}_\alpha{}^{\mathrm{HF}}$. Equation (7a) demonstrates clearly the conditions under which self-consistent orbitals satisfy the HF theorem: $\vec{F}_\alpha{}^{\mathrm{IBS}}$ vanishes either for the original HF condition that ψ be an exact eigenstate $(\hat{H} - \epsilon_j)|\psi_j\rangle = 0$, or for the far weaker condition that the basis functions χ expanding ψ have no dependence on the nuclear coordinates (i.e., $d\chi/d\vec{R} = 0$, like in a "floating basis," such as plane waves,[11] or one-center orbitals[9]). Equation (7a) further shows that the best strategy for obtaining good approximations to $\vec{F}_\alpha{}^{\mathrm{HF}}$ if reasonably complete atom-anchored basis orbitals are used is to include along with the most significantly admixed (large a_{ji}) basis orbitals χ_i the three partial derivatives $\chi_i' = \partial\chi_i/\partial\vec{r}$; this will diminish the error due to the original χ_i, since the variational coefficients of χ_i' are small. Hence, the reason that monomial Gaussian basis functions χ can give better results for forces than other atom-anchored bases which produce comparable total energies[5] is that the χ' are also monomial Gaussian and are easily included in the basis.

The importance of $\vec{F}_\alpha{}^{\mathrm{IBS}}$ can be illustrated by considering a spherical neutral atom in a uniform electric field $\vec{E}$. By Eq. (6), $\vec{F}_\alpha{}^{\mathrm{HF}} = eZ_\alpha\vec{E}$ if $\rho(\vec{r})$ is assumed to remain undeformed. The correct electrostatic result is $\vec{F}_\alpha^{\mathrm{HF}}=0$. In reality, a small field-induced distortion of $\rho(\vec{r})$ will cancel exactly the nuclear force $eZ_\alpha\vec{E}$. In the present formulation, the force $\vec{F}_\alpha^{\mathrm{IBS}}$ of Eq. (7a) will correct the first-order error of $\vec{F}_\alpha^{\mathrm{HF}}$ due to the charge distortion (polarization) effect. Equation (7a) likewise shows that frozen-core approximations will produce very poor forces,[12] since a frozen (non-self-consistent) core density is made from wave functions lacking the variational freedom to respond to the potential of the polyatomic system. Notice, however, that in pseudopotential calculations[11] the core orbitals are eliminated altogether from the spectrum by interpreting the external potential v_α in Eq. (6) as a pseudopotential. The force exerted by the core can then be expressed as a new term[13] in $\vec{F}_\alpha^{\mathrm{HF}}$. This, as well as the fact that $\vec{F}_\alpha^{\mathrm{IBS}}\equiv 0$ for a plane-wave basis used in such calculations, explains the numerical precision of recent pseudopotential force computations.[11] We note that similar considerations apply if one seeks derivatives of E with respect to an electric field (yielding polarizabilities) or a magnetic field (yielding susceptibilities).

The expression (7b) for $\vec{F}_\alpha^{\mathrm{NSC}}$ demonstrates the large first-order sensitivity of the forces to imperfections in self-consistency, an observation recently reported in computational studies.[11] The force $\vec{F}_\alpha^{\mathrm{NSC}}$ has been described previously by Pickett[14] in the context of plane-wave pseudopotential calculations. However, this quantity is difficult to calculate because it requires knowing the response of the charge density to motion of each nucleus in each direction. Fortunately, as we will show below, the problem can be transformed so that this term need not be calculated.

Transformation of forces.—The necessary conditions for a minimum of $E[\vec{R}_\alpha,\rho]$ are given by Eqs. (5) and (8). We have formulated the problem so that one can simply transform these equations into an equivalent set that has the same solutions but does not require the evaluation of $\vec{F}_\alpha^{\mathrm{NSC}}$. This is done by recognizing that the departure of U from V_{KS} controls the NSC force [Eq. (7b)] and the density force [Eq. (4)] in exactly the same way. Hence, if one imposes the conditions for simultaneous equilibrium,

$$\begin{aligned}&\nu(\vec{\mu},\vec{R})-\vec{\mu}=0,\\&\vec{F}_\alpha^{\mathrm{HF}}(\vec{\mu},\vec{R})+\vec{F}_\alpha^{\mathrm{IBS}}(\vec{\mu},\vec{R})=0,\end{aligned}\tag{9}$$

then when Eq. (9) (where $\vec{F}_\alpha^{\mathrm{NSC}}$ does not appear) is satisfied, so are Eqs. (5) and (8). The problem of a simultaneous relaxation of nuclei and densities has been reduced therefore to a system of simultaneous equations (9) and can be solved by any one of the many available methods. We have recently demonstrated that Broyden method (a modification of the the Newton-Raphson method in which the Jacobian is approximated with use of information from the iteration history; cf. Ref. 7 and references therein) is useful for the simpler problem of self consistency. It may also work for the present problem. The present force-relaxation method can make *simultaneous improvements* in all the variables, the potential and the atomic positions. The Jacobian[7] is constructed through the iteration history both for the potential parameters $\vec{\mu}$ and for the nuclear coordinates $\vec{R}$. It hence can change both types of variables in each iteration, in contrast to the consecutive indirect methods[1] that change only one type of parameter at a time. Furthermore, the present approach requires computation of only the generalized forces of Eq. (9); it "remembers" information from past iterations, and is able to use this information as a guide toward the minimum. The present force-relaxation method opens the way for studying the electronic properties of systems with experimentally unknown atomic geometries.

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