PHYSICAL REVIEW A **76**, 062512 (2007)

# Alternative perspective on density-functional perturbation theory

Brett I. Dunlap
*Code 6189, Theoretical Chemistry Section, U.S. Naval Research Laboratory, Washington, D.C. 20375-5342, USA*

(Received 5 June 2007; published 26 December 2007)

Perturbation theory is examined in analytic density-functional theory (ADFT), for which $V$ representability means slightly more than in conventional density-functional theory because the potential is fitted. There is synergism between variationality and $V$ representability. Together they redirect the object of perturbation theory from the set of occupied virtual orbital rotations to the change in the fit to the Kohn-Sham potential, which is called the Sambe-Felton potential. This reduces the dimensionality of perturbation theory from order $N^2$ to order $N$, where $N$ is the number of basis functions. With variational fitting, no fractional or negative powers of the density appear when using the Slater exchange kernel, which is proportional to the cube root of the spin density. Requiring the Fock matrix and density matrix to commute through each order of perturbation theory determines the role of fractional occupation numbers in density-functional perturbation theory, which are treated via the corresponding nonintegral differences between the occupation numbers of orbitals. This theory is tested by removing a tenth or twentieth of an electron from the highest occupied molecular orbital for a standard set of small molecules, in which case the first- and second-order perturbed energies are accurate to 70%, when compared to the energy difference of the two corresponding self-consistent-field (SCF) calculations. For an all-electron ADFT calculation on a $C_{4v}$-symmetric $Zr_6O_{12}$ cluster, the timing for all SCF coupled perturbed iterations is not significant compared to the single required $N^4$ sum over occupied and virtual orbitals.

DOI: 10.1103/PhysRevA.76.062512 PACS number(s): 31.15.Ew, 03.65.Fd, 31.15.Md

## I. INTRODUCTION

Analytic density-functional theory (ADFT) is the subset of density-functional theory [1] that can be treated without numerical integration. In advocating the Gaussian orbital basis for Hartree-Fock (HF) calculations, Boys noted that this quantum chemistry does not depend on any numerical integration process [2]. Numerical integration breaks rotational invariance in DFT [3]. As a consequence, the fractional-occupation-number (FON) problem of DFT, which requires all partially occupied orbitals to have precisely the same eigenvalue [4], becomes dependent on the orientation of the degenerate molecular orbitals within the molecule. In contrast, analytic HF computer codes gave molecular energies to machine precision when Boys' vision was realized in no small measure through the work of Pople and collaborators [5]. Also in contrast to numerical DFT, all derivatives of the ADFT potential-energy surface are smooth [6]. Almost simultaneously with Boys, however, Slater simplified HF theory [7] through what, with the advent of DFT, has come to be called the Kohn-Sham (KS) [8] potential. If approximating molecular orbitals as linear combinations of atomic orbitals (LCAO) is a good idea, then fitting the KS potential as linear combinations of atomic potentials (LCAP) should also be a good idea [9]. In this work a fit of the KS potential to a LCAP will be called a Sambe-Felton (SF) potential. Pople and co-workers call the difference between the KS and SF potentials projection [10]. The smaller variational space of the SF potential is exploited in this work. The LCAP coefficients will be said to comprise the SF vector.

A necessary prerequisite for computing stationary, machine-precision DFT energies is that there be a fully variational connection between the energy and the KS potential. In the LCAO approach this variational connection defines a variational SF potential [11]. A descendent of our original code, DGAUSS, used this variational fitting of the Coulomb part of the SF potential [12]. Its derivatives were imprecise, because it did not fully take into account the derivative of the fit to the exchange-correlation part of the SF potential. Instead both the exchange-correlation energy and potential were independently fitted [13]. In a later version of DGAUSS, fits were used only in the SF potential, and numerical integrals were used to compute the first derivative of the exchange energy [12]. Precise, fitted first derivatives are possible, but the full derivative of energy with respect to an orbital, via the chain rule through the fitting equations, introduces numerical Fock-matrix components that are not of SF form [14]. Today, essentially all electronic-structure computer codes treat the exchange-correlation term of the KS potential numerically.

By considering all occupied virtual orbital rotations, precise derivatives were added to DGAUSS along with four-index, two-electron integrals. In this approach, DFT is necessarily as slow as *ab initio* codes, even when using variational fitting [15]. This approach to DFT response functions continues [16], even though, as will be shown, it is dimensionally impossible that the independent mixing of each occupied orbital with each virtual orbital is $V$ representable [17,18]. Time-dependent perturbation theory, which in principle can excite an electron from any occupied orbital to any virtual orbital [19], may require orbital ($\mathbf{u}$) perturbation theory and is not considered here.

The alternative method for computing derivatives is simply to take the derivatives of the energy plus Lagrange multipliers times the constraint equations term by term [20]. ADFT has no four-index matrix elements and thus has precise first derivatives at $N^3$ cost [21]. If the KS potential is fitted to SF form using roughly the same number of basis functions as the number $N$, used to fit the orbitals, then the dimensionalities of $V$ representable perturbation ($V$ perturbation) and $\mathbf{u}$ perturbation theory differ. The space of orbital rotations has dimension $N^2$, while the space of all fitted Fock potentials has roughly dimension $N$. Thus for bulk materials HF is rather impractical, as Slater noted, so $V$-representable molecular perturbation theory is consistent with perturbation theory for crystals as it is practiced [22]. In variational perturbation theory, the first-order changes in the occupied orbitals can be individually varied to minimize the second-order energy in sequence and the whole process repeated iteratively to optimize the perturbed energy [23]. In ADFT additional variational principles on the SF potential give the first-order change in the potential directly. Furthermore, ADFT is analytic and finite in every respect.

To my knowledge ADFT is the only electronic quantum mechanics with order-$N$ static perturbation theory as is shown for one simple functional and one simple perturbation. The full KS and thus SF potential is invariant under all group operations and thus its length can be reduced by as much as the order of the point group that leaves the perturbation and molecule invariant. While a general perturbation will break molecular symmetry, some perturbations do not and will be treated most efficiently in $V$ perturbation theory. One perturbation that preserves symmetry is changing the number of electrons in an orbital by a small nonintegral amount. The second derivative of the energy with respect to orbital occupation number is computed in this work. This is a necessary first step in solving the FON problem using perturbation theory. Section II develops FON perturbation theory in ADFT. Section III computes the second derivative of the ADFT energy of a standard set of molecules with respect to highest-occupied-molecular-orbital (HOMO) occupation number and the larger $C_{4v}$-symmetric $Zr_6O_{12}$ cluster. The last section contains a few concluding remarks.

## II. ADFT PERTURBATION THEORY

After solving for the molecular orbitals, the ADFT energy can be expressed as

$$\begin{aligned} E(\mathbf{n},\mathbf{u},c,x,y) &= \sum_{i\mu\nu} (n_i C^{i*}_{\mu} F_{\mu\nu} C^{i}_{\nu}) - \frac{1}{2}\langle c|c\rangle \\ &\quad - \kappa\left\langle -\frac{2}{3}xxy + \frac{1}{3}yy\right\rangle \\ &= \sum_{i} (n_i \varepsilon_i) - \frac{1}{2}\langle c|c\rangle \\ &\quad - \kappa\left\langle -\frac{2}{3}xxy + \frac{1}{3}yy\right\rangle, \end{aligned} \tag{1}$$

where $\kappa = \frac{9}{8}\left(\frac{3}{\pi}\right)^{1/3}\alpha$ (for a spin-polarized calculation) and $\alpha$ is Slater's exchange parameter, the $C^{i}_{\mu}$ are LCAO coefficients, $F_{\mu\nu}$ is the Fock matrix, made up of one-electron terms and three-center exchange integrals, indicated by angular brackets, and Coulomb integrals, indicated by an additional vertical line separating the charges. The LCAP functions $c(\mathbf{r})$, $\mathbf{x}(\mathbf{r})$, and $y(\mathbf{r})$ are obtained from the calculus of variation applied to the entire ADFT energy [24]. The second line gives the energy in terms of the sets of molecular orbital occupation numbers and eigenvalues $\{\varepsilon_i\}$, and two terms that robustly correct for the overcounting of Coulomb and exchange energies in the sum of the eigenvalues. The connection between orbitals and SF potential also holds for perturbed DFT orbitals, if the perturbed orbitals are also $V$ representable. In ADFT this means that *all* orbitals through *all* orders of perturbation theory are each generated by a pair of vectors $\mathbf{c}$ and $\mathbf{x}$ through the corresponding order of perturbation theory. In practice these SF potentials have dimension that is approximately $2N$. If the calculation is spin polarized and all degrees of freedom are active, then the length of the perturbation vector is $6N$. On the other hand, assuming 10% of the orbitals are occupied, then the $\mathbf{u}$ perturbation vector has length $0.09N^2$. For this example, $V$ perturbation theory becomes more efficient than $\mathbf{u}$ perturbation theory for $N > 66$.

The simplest symmetric perturbation is the self-consistent-field (SCF) process itself. Before a variational fitting method for exchange was found, perturbation theory was applied to the connection between $c$ and the set of molecular orbitals [25]. This limited perturbation theory is effective because, given a set of orbitals and a SF potential that do not correspond, then correcting $c$ will destabilize the current set of orbitals relative to a nearby set, because variational fitting necessarily increases the Coulomb repulsion of the current set of orbitals [11], whereas changing the exchange potential will do little because the cube root functional makes any non-negative function such as the density smoother than it originally was. The smoother the exchange kernel is, the more all normalized orbitals experience equal exchange expectation values. A complete ADFT perturbation theory should, nevertheless, prove even more useful.

It is useful to define $R^{1}_{ij}$ to be the expansion coefficient of the first-order orbitals in terms of the zeroth-order orbitals [26],

$$\mathbf{C}^{(1)} = \mathbf{R}^{(1)} \cdot \mathbf{C}^{(0)}, \tag{2}$$

where the $\mathbf{C}$ with superscripts are the LCAO coefficients of Eq. (1) at each order of perturbation theory. The perturbed orbitals are generated by the sum of the SF potentials through each order. Expanding the first-order orbitals $u_i$ in terms of the zeroth-order orbitals and then projecting with the same zeroth-order orbital gives the shift in the eigenvalues,

$$\varepsilon^{(1)}_{i} = \Delta\mathbf{c} \cdot \mathbf{C}_{ii} - \Delta\mathbf{x} \cdot \mathbf{X}_{ii} + V_{ii}, \tag{3}$$

where $\Delta c$ and $\Delta x$ are the change in Coulomb and exchange LCAP coefficients, respectively, $ii$ indicates a diagonal matrix in the zeroth-order set of eigenvalues, and $V$ is the external perturbation on the electrons. For perturbations that create only real expansion coefficients, projecting with all other zeroth-order orbitals involves the transformation matrix

$$\Delta\mathbf{c} \cdot \mathbf{C}_{ij} - \Delta\mathbf{x} \cdot \mathbf{X}_{ij} + V_{ij} = (\varepsilon_i - \varepsilon_j) R^{(1)}_{ij}, \tag{4}$$

where these eigenvalues are zeroth order. This is solved for the transformation matrix,

$$R_{ij}^{(1)} = (\Delta\mathbf{c}\cdot\mathbf{C}_{ij} - \Delta\mathbf{x}\cdot\mathbf{X}_{ij} + V_{ij})/(\varepsilon_i - \varepsilon_j), \tag{5}$$

where for integral occupation numbers orbital $i$ is occupied and $j$ is empty or virtual. This depends on not only the perturbation, but also the change in SF potential [27]. Second-order perturbation theory gives the sum of the occupied perturbed orbital eigenvalues through second order,

$$n_i(\varepsilon_i + \varepsilon_i^{(1)} + \varepsilon_i^{(2)}) = n_i(\varepsilon_i + V_{ii}) + \langle\rho|\mathbf{c}\rangle\cdot\Delta\mathbf{c} - \frac{4}{3}\kappa\langle\rho\mathbf{x}\rangle\cdot\Delta\mathbf{x} + \sum_j w_{ij}(\Delta\mathbf{c}\cdot\mathbf{C}_{ij} - \Delta\mathbf{x}\cdot\mathbf{X}_{ij} + V_{ij})^2, \tag{6}$$

where $w_{ij}$ is to be determined for the case of fractional occupation numbers. In the limit of integral occupancy, this sum over $j$ is limited to virtual orbitals and $w_{ij}$ is known,

$$w_{ij} \approx w_{ij0} = \frac{\delta(n_i - 1)\,\delta(n_j)}{\varepsilon_i - \varepsilon_j}, \tag{7}$$

where the Dirac $\delta$ functions ensure that levels are either occupied by one electron or empty. The sum of the perturbed orbital eigenvalues is part of the total perturbed ADFT energy,

$$\begin{aligned} E[\rho,c,x,V,\Delta c,\Delta x] &= E^{(0)} + E^{(1)} + E^{(2)} \\ &= \langle\rho|\mathbf{c}\rangle\cdot\Delta\mathbf{c} - \frac{4}{3}\kappa\langle\rho\mathbf{x}\rangle\cdot\Delta\mathbf{x} - \frac{1}{2}\langle c+\Delta c|c+\Delta c\rangle \\ &\quad + \frac{1}{3}\kappa\langle(x+\Delta x)(x+\Delta x)\mathbf{y}\rangle\cdot\langle\mathbf{yy}\rangle^{-1}\cdot\langle(x+\Delta x)(x+\Delta x)\mathbf{y}\rangle \\ &\quad + \sum_i n_i(\varepsilon_i + V_{ii}) + \sum_{ij} w_{ij}(\Delta\mathbf{c}\cdot\mathbf{C}_{ij} - \Delta\mathbf{x}\cdot\mathbf{X}_{ij} + V_{ij})^2, \end{aligned} \tag{8}$$

where $\rho$ is the zeroth-order charge density (given by the occupation numbers, $\mathbf{c}$, and $\mathbf{x}$), and the exchange energy of Eq. (1) has been made stationary via an unconstrained variation of $\mathbf{y}$. In the following the inverse $\mathbf{y}$ overlap matrix is removed by transforming to the Löwdin-orthogonalized basis $\bar{\mathbf{y}}$. Making this energy stationary with respect to $\Delta c$ and $\Delta x$ is equivalent to solving the coupled perturbed KS equations because this is the full second-order energy. The number of apparent unknowns is reduced by 2 by denoting the original SF potential by a zero subscript,

$$\begin{aligned} E^{(0)} + E^{(1)} + E^{(2)} &= \sum_i n_i(\varepsilon_i + V_{ii}) + \langle\rho|\mathbf{c}\rangle\cdot(\mathbf{c}-\mathbf{c}_0) - \frac{4}{3}\kappa\langle\rho\mathbf{x}\rangle\cdot(\mathbf{x}-\mathbf{x}_0) \\ &\quad + \sum_{ij} w_{ij}[(\mathbf{c}-\mathbf{c}_0)\cdot\mathbf{C}_{ij} - (\mathbf{x}-\mathbf{x}_0)\cdot\mathbf{X}_{ij} + V_{ij}]^2 \\ &\quad - \frac{1}{2}\langle c|c\rangle + \frac{1}{3}\kappa\langle xx\bar{\mathbf{y}}\rangle\cdot\langle\bar{\mathbf{y}}xx\rangle. \end{aligned} \tag{9}$$

The density is not subscripted, even though it is constructed from unperturbed orbitals, to allow for the case where the perturbation is itself a change in occupation numbers.

Differentiating this second-order energy with respect to $c$ gives the perturbed charge-density fit,

$$\langle\mathbf{c}|\mathbf{c}\rangle\cdot\mathbf{c} = \langle\rho|\mathbf{c}\rangle + \sum_{ij} 2w_{ij}\mathbf{C}_{ij}[(\mathbf{c}-\mathbf{c}_0)\cdot\mathbf{C}_{ij} - (\mathbf{x}-\mathbf{x}_0)\cdot\mathbf{X}_{ij} + V_{ij}]. \tag{10}$$

If we view this equation as an equation for variationally fitting the total charge density [11],

$$\langle\mathbf{c}|\mathbf{c}\rangle\cdot\mathbf{c} = \langle\rho + \Delta\rho|\mathbf{c}\rangle, \tag{11}$$

then the change in density is expressed as

$$\Delta\rho(\mathbf{r}) = 2\,\mathrm{Re}\left(\sum_{ij} w_{ij}\phi_i^*[(\mathbf{c}-\mathbf{c}_0)\cdot\mathbf{C}_{ij} - (\mathbf{x}-\mathbf{x}_0)\cdot\mathbf{X}_{ij} + V_{ij}]\phi_j\right). \tag{12}$$

This becomes the standard expression for the perturbed density [22,27] upon substituting $w_{ij0}$ for $w_{ij}$. Both $\Delta\rho$ and $\Delta c$ are functions of the perturbation, and must be solved for self-consistently. Setting $\Delta\mathbf{x}=\mathbf{0}$, $V_{ij}=0$, restricting the $i$ to be the highest occupied molecular orbital and $j$ to be the lowest unoccupied orbital of each symmetry, solving for $\Delta\mathbf{c}$, and then scaling it down by a mixing parameter yields our convergence accelerator [25], which is used until direct iteration on the iterative subspace (DIIS) is turned on. If one is starting from a converged SCF calculation, then $\langle\mathbf{c}|\mathbf{c}\rangle\cdot\mathbf{c}_0=\langle\rho|\mathbf{c}\rangle$.

A Newton-Raphson step toward making the second-order energy stationary with respect to the change in exchange fit is expressed as

$$\begin{aligned} \mathbf{W}_2(x)\cdot(\mathbf{x}-\mathbf{x}_0) &= -\mathbf{W}_1(x) + \frac{4}{3}\kappa\langle\rho\mathbf{x}\rangle + 2\sum_{ij} w_{ij}[\mathbf{X}_{ij}(\mathbf{c}-\mathbf{c}_0)\cdot\mathbf{C}_{ij} \\ &\quad - (\mathbf{x}-\mathbf{x}_0)\cdot\mathbf{X}_{ij} + V_{ij}], \end{aligned} \tag{13}$$

where

$$\mathbf{W}_1(x) = \frac{4}{3}\kappa\langle\mathbf{x}x\bar{\mathbf{y}}\rangle\cdot\langle\bar{\mathbf{y}}xx\rangle \tag{14}$$

and

$$\mathbf{W}_2(x) = \frac{4}{3}\kappa\langle\mathbf{xx}\bar{\mathbf{y}}\rangle\cdot\langle\bar{\mathbf{y}}xx\rangle + \frac{8}{3}\kappa\langle\mathbf{x}x\bar{\mathbf{y}}\rangle\cdot\langle\bar{\mathbf{y}}x\mathbf{x}\rangle. \tag{15}$$

The vector $-\mathbf{W}_1(x)+\frac{4}{3}\kappa\langle\rho\mathbf{x}\rangle$ is zero if one is perturbing a SCF solution. The identity Eq. (12) transforms Eq. (13) into the Newton-Raphson step [24],

$$\mathbf{W}_2(x)\cdot(\mathbf{x}-\mathbf{x}_0) = -\mathbf{W}_1(x) + \frac{4}{3}\kappa\langle(\rho+\Delta\rho)\mathbf{x}\rangle, \tag{16}$$

toward variationally fitting $x$ to $(\rho+\Delta\rho)^{1/3}$.

Suppose the perturbation is linear in some parameter, such as the electric field. Let an overdot represent a derivative with respect to that parameter. The variational coupled perturbed equations (10) and (13) are linear in the SF potential and its derivatives. In this case the second-order energy is simply expressed as

$$\frac{1}{2}\ddot{E} = \frac{1}{2}\sum_{ij} w_{ij}(\dot{\mathbf{c}} \cdot \mathbf{C}_{ij} - \dot{\mathbf{x}} \cdot \mathbf{X}_{ij} + \dot{V}_{ij})^2 - \frac{1}{2}\langle \dot{c}|\dot{c}\rangle + \frac{1}{3}\kappa\langle \dot{x}\dot{x}\overline{\mathbf{y}}\rangle \cdot \langle \overline{\mathbf{y}}xx\rangle + \frac{2}{3}\kappa\langle \dot{x}x\overline{\mathbf{y}}\rangle \cdot \langle \overline{\mathbf{y}}\dot{x}x\rangle, \qquad (17)$$

where the derivatives of the SF potential are the solution of the derivatives of the algebraic coupled perturbed equations. For finite perturbations, however, these equations require self-consistent solution.

DIIS is the most effective method for speeding SCF convergence. Given a new set of molecular orbitals obtained from the eigenvalue problem, a density is generated and a set of previous Fock matrices is mixed to best commute with that density [28],

$$\mathbf{FDS} - \mathbf{SDF} = \mathbf{0}, \qquad (18)$$

where $\mathbf{D}$ is the density matrix and $\mathbf{S}$ is the overlap matrix. The density and Fock matrices also commute if there are fractionally occupied orbitals and the density is not idempotent,

$$\mathbf{DD} \neq \mathbf{D}. \qquad (19)$$

The densities for converged HF solutions are always idempotent; however, for certain bond distances and multiplicities in DFT no self-consistent, idempotent solutions exist [4]. In order to understand those somewhat rare cases, it is convenient to study standard molecules ionized nonintegrally. The remainder of this work considers a change in a single occupation number and no external perturbing potential, $V=0$.

With any perturbation, the SF potential changes by an amount

$$\Delta\mathbf{F}_{ij} = \mathbf{c} \cdot \Delta\mathbf{C}_{ij} - \mathbf{x} \cdot \Delta\mathbf{X}_{ij}. \qquad (20)$$

In the unperturbed basis, the foundation of DIIS, Eq. (18) is the statement that the density and Fock matrices commute [29],

$$[\mathbf{F} + \Delta\mathbf{F}, \mathbf{D} + \Delta\mathbf{D}]_{ij} = \sum_k (F + \Delta F)_{ik}(D + \Delta D)_{kj} - (D + \Delta D)_{ik}(F + \Delta F)_{kj} = 0. \qquad (21)$$

To zero order these matrices commute if we have a SCF solution of the unperturbed problem. In the unperturbed basis Eq. (12) requires that the elements of the first-order Fock and density matrices be proportional,

$$\Delta D_{ij}^{(1)} = w_{ij}\Delta F_{ij}, \qquad (22)$$

where the factor of 2 is absorbed by assuming that these matrices are Hermitian. The density and Fock matrices are diagonal in the unperturbed basis. In that basis, the density and Fock matrices commute through first order, provided that

$$\varepsilon_i w_{ij}\Delta F_{ij} + \Delta F_{ij}n_j - w_{ij}\Delta F_{ij}\varepsilon_j - n_i\Delta F_{ij} = 0, \qquad (23)$$

where these are the total, through first-order, perturbed occupation numbers, or

$$w_{ij} = \frac{n_i - n_j}{\varepsilon_i - \varepsilon_j}, \qquad (24)$$

which is consistent with Eq. (7) for integral occupation numbers, but is symmetric in the two orbitals. It is zero if both levels are either fully occupied or completely empty. As each level of perturbation theory affects all higher levels there are many consequences of any modification [30]. Given this apparently new equation, the new second-order energy,

$$E^{(2)} = \mathrm{Tr}(\Delta\mathbf{D}\Delta\mathbf{F}) = \sum_{ij} \frac{n_i - n_j}{\varepsilon_i - \varepsilon_j}|\Delta F_{ij}|^2, \qquad (25)$$

is consistent with Eq. (6). Note that neither these equations nor the commutator of the Fock and density matrices single out occupied or virtual spaces, but it is unnecessary to compute perturbed empty orbitals and mixing among the occupied orbitals [31].

In general, the changes in SF potential and second-order energy are generated from the solution of a set of nonlinear equations of dimension that is the length of $\mathbf{c}$ plus the number of spins times the length of $\mathbf{x}$. For the case of geometry optimization in $\mathbf{u}$ perturbation theory, the elegant $Z$-vector method of Handy and Schaefer [32] solves for a single vector of length the number of occupied orbitals times the number of virtual orbitals, independent of nuclear displacement. If roughly 10% of the orbitals are occupied this product can be $0.1N^2$, where $N$ is the size of the orbital basis. In $V$ perturbation theory, solving Eqs. (10) and (13) generates roughly $6N$ numbers for each of the three nuclear degrees of freedom. In this case, if the orbital basis set averages fewer than 180 functions per atom, which includes practically all orbital basis sets, then the amount of numbers generated in $\mathbf{u}$ perturbation for geometry optimization is less than that in $V$ perturbation theory, but the latter can be generated sequentially or in parallel fashion for each displacement using matrices containing $\sim N^2$ elements. The Green's function in HF theory is a vector, but in $V$ perturbation theory it is a matrix.

For the case of occupation-number changes and no external potential, it is convenient to develop a combined notation for the fit,

$$\mathbf{f} \equiv \begin{pmatrix} \mathbf{c} \\ \mathbf{x} \end{pmatrix}. \qquad (26)$$

The first-order expectation values of the fitting basis functions can be evaluated using the expression for the perturbed density, Eq. (12),

$$\langle \Delta\rho\mathbf{f}\rangle = \mathbf{F} \cdot \mathbf{f}, \qquad (27)$$

where

$$\mathbf{F} = \sum_{ij} w_{ij}\begin{pmatrix} \mathbf{C}_{ij} \\ -\mathbf{X}_{ij} \end{pmatrix}(\mathbf{C}_{ij}, -\mathbf{X}_{ij}) + \begin{pmatrix} \langle \mathbf{c}|\mathbf{c}\rangle & 0 \\ 0 & -\mathbf{W}_2 \end{pmatrix}. \qquad (28)$$

The single summation over orbital pairs in the above equation completely removes all the orbitals from the coupled perturbed SF problem. Of course this is challenging because this sum is order $N^4$. It is parallelized by distributing pairs of atoms to the processors, and having each processor compute all zeroth-order molecular orbital matrix elements of fitting functions on the two centers. After this single summation, the coupled set of equations for the fits, Eqs. (12) and (16), can be solved iteratively,

$$\mathbf{f}_{n+1} = \mathbf{F}^{-1} \cdot \langle \Delta\rho \mathbf{f}_n \rangle, \tag{29}$$

with damping, which is used in the following.

## III. APPLICATION

In HF theory, particularly for finite systems, there is a tendency toward integral occupation numbers because the occupied orbitals experience a potential only due to all the other electrons while virtual orbitals are repelled by all the electrons. Nonintegral occupation numbers are fairly common in DFT and are useful for treating the breaking and making of some chemical bonds and the crossing of even doubly excited electronic configurations [4,33–35]. The most algorithmically challenging perturbation is the case of a change in occupation number during the SCF process. That process is perturbed by a change in occupation numbers,

$$n_i \to n_i + \Delta n_i, \tag{30}$$

subject to charge conservation,

$$\sum_i \Delta n_i = 0. \tag{31}$$

At this point, it is convenient to consider only a single change in occupation number.

In DFT the molecular orbital eigenvalues are the first derivatives of the energy with respect to orbital occupation number [36]. Thus the first-order energy change corresponding to Eq. (30) is expressed as

$$E^{(1)} = \varepsilon_i \Delta n_i. \tag{32}$$

This expression can be tested and perhaps improved upon by second-order perturbation theory using Becke's test set of 56 small molecules [37]. The geometry of each molecule is optimized using two sets of basis functions. The smaller basis set combination is the DGAUSS double-$\zeta$ plus polarization (DZP) orbital basis set named DZVP2 [12]. The non-$s$ fitting functions for this orbital basis are the charge-density fitting functions of the A2 set developed for this orbital basis set [38]. The bigger orbital basis set used is 6311G$^{**}$ [39,40], which is a triple-$\zeta$ plus polarization basis set (TZP). The non-$s$ fitting functions for this orbital basis are from the resolution-of-the-identity-$J$ charge-density fitting basis for another TZP orbital basis [41]. Both $s$-fitting basis sets are obtained by scaling each primitive $s$-orbital exponent by 2 for the density fit, 2/3 for the **x** basis, and 4/3 for the **y** basis and both fits are constrained [24] for the geometry optimization. A single functional is used for both basis sets. It gives exact experimental atomic energies when using the TZP basis [42]. With this functional and the larger basis set, molecules dissociate into atoms having their correct experimental energies.

At the optimized geometries the occupancy of the HOMO is reduced by a quarter, i.e., by half an electron if the orbital is doubly occupied. Constraints on the fits are turned off to avoid Lagrange multipliers. In that case, the SCF energy using the initial occupation numbers and Eq. (32) give the energy through first order ($E^{(0)}+E^{(1)}$) for adding a tenth of an electron back into the HOMO, or a twentieth of an electron if the molecule is treated via a spin-polarized calculation.

A second estimate of the final energy is given by variation of Eq. (9), and is accurate through second order in perturbation theory. The variational energy can be obtained by iterating Eq. (29), if it converges. In this work only simple mixing is tested. For SCF calculations on this set of 56 molecules, reliable starting mixing parameters for the amount of each new SF vector to be mixed with the old range from 0.4 to 0.7 for the charge density fit and are one-tenth more for the exchange part of the SF vector. The convergence properties of Eq. (29) are significantly worse. A solution for the variational second-order energy can be obtained for all the molecules of Becke's set except CN, HCO, and NO by starting with a mixing parameter of a quarter of the charge density SCF mixing parameter and increasing in steps up to the exchange SCF mixing parameter. If a convergent process can be started, then convergence is uniform upon reaching the exchange SCF mixing parameter, unlike the SCF process itself, which stalls under simple mixing [20]. The iterative process is ended when a norm on the change in the first-order SF vector is less than $10^{-9}$, like the norm on the SCF process for geometry optimization. All energies are well converged when this norm is less than $10^{-4}$. No iterative process based on using the fully coupled Eq. (29) will work for the three molecules CN, HCO, and NO, which are spin polarized and contain first-row atoms to the right of the periodic table. Obtaining a converged quadratic perturbed energy for them will require uncoupled fitting of the charge density and exchange for each spin and is not further studied in this work.

The exact answer for adding fractional electrons to a molecule is the difference between the SCF energies for calculations using the two different orbital occupancies, which is called the ΔSCF energy. These two approximate energies are compared with the ΔSCF energy in Table I. For this case of small changes in occupancy, the second-order energy reduces the error of only using the first-order energy, Eq. (32), by 71% on average for both basis sets. The error reduction is slightly more for the largest change, which occurs for the hydrogen fluoride molecule for both basis sets.

The timings for this set of molecules are not significant. Appropriate to atomistic simulations of solid oxide fuel cells, this theory has been applied to the change in occupation numbers for a $C_{4v}$-symmetric $Zr_6O_{12}$ cluster, which is the three-formula-unit piece of the high-temperature, cubic phase of zirconia. ADFT becomes singular if the Zr and O $\alpha$ values are significantly different, so a single, optimal, $\alpha$ value of 0.698 was used [43]. In an all-336-electron calculation using the DGAUSS combinations of basis and fitting functions, this cluster has a rather small, ~2 eV, gap between the HOMO and the lowest occupied molecular orbital. The coupled perturbed SCF step is essentially a matrix multiplication, Eq. (29), and the required 87 iterations take 50 s on a single titanium processor. This amount of time is taken as the appropriate unit of time in the following. The single $N^4$ sum-

TABLE I. The error in total energy in electron volts relative to ΔSCF calculations estimated by first- and second-order perturbation theory for adding a small fraction of an electron to a partially emptied HOMO for a set of 53 molecules (see text). In this case the second-order energy $E^{(2)}$ is about 70% of the error in using Janak's theorem [36] alone (second column in each set).

| | Basis | | | | | |
|---|---|---|---|---|---|---|
| | DZP | | | TZP | | |
| Energy order | ΔSCF | $E^{(1)}-\Delta$SCF | $E^{(1)}+E^{(2)}-\Delta$SCF | ΔSCF | $E^{(1)}-\Delta$SCF | $E^{(1)}+E^{(2)}-\Delta$SCF |
| Average energy (eV) | −1.0893 | 0.0402 | 0.0115 | −1.0794 | 0.0405 | 0.0117 |
| Maximum energy (eV) | −2.4771 | 0.0873 | 0.0240 | −2.4839 | 0.0879 | 0.0242 |

mation takes 20 time units. This is longer than need be for a single processor, because the three-center integrals are recomputed rather than being read from its disk. The alternative nondirect, disk-read, calculation would be efficient for low numbers of processors, but require large amounts of data transfer if a large number of processors were used. In this calculation the 30 energy-SCF steps required a total of three time units. A single geometry optimization step requires 21 time units. This calculation unlike the previous calculations constrained the charge-density and exchange fits. This makes the first- plus second-order energy 94% of the total ΔSCF energy.

## IV. CONCLUSION

The linear response of the density-functional theory envisioned by Sambe and Felton is quite simple and powerful. With unfitted Slater-type functionals, $\delta E_x = -\kappa\langle\rho^{1/3}\delta\rho\rangle$ contains the $1/3$ power of the density, but no fractional powers of the density appear in the above equations. The second variation of the unfitted approach, which involves $-2/3$ of the density, is infinitely attractive wherever there are no electrons—practically everywhere for a finite molecule. Second-order properties are straightforward in ADFT, although convergence problems remain to be investigated for a few light, spin-polarized molecules.

ADFT perturbation theory scales linearly with the size of the molecule. In contrast, the conventional approach to perturbation theory is based on orbital rotations between the occupied and virtual spaces. These transformations scale as the square of the size of the system, for the size of systems that are tractable, without additional approximations, today [44].

Perturbation theory has been extended to fractional occupation numbers and shown to be rather accurate for small changes in molecular HOMO occupations. Instead of dividing orbitals into occupied and virtual orbitals, this approach involves the difference in orbital occupancy divided by the difference in eigenvalues, which is symmetric in any two orbitals and vanishes if the two orbitals have exactly the same occupancy. Thus a fractionally occupied orbital at the Fermi level acts as both an occupied level and as a virtual level in $V$ perturbation theory. We expect to modify slightly this occupation-number perturbation theory to find nearby, low-lying, singlet-diradical states in molecular dynamics calculations of hypervelocity chemistry involving singlet-state reactants.

## ACKNOWLEDGMENTS

Discussions with Shashi Karna and Carter White about perturbation theory are greatly appreciated. The Office of Naval Research, directly and through the Naval Research Laboratory, supported this research.

[1] W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
[2] S. F. Boys, Proc. R. Soc. London, Ser. A **200**, 542 (1950).
[3] B. G. Johnson and M. J. Frisch, Chem. Phys. Lett. **216**, 133 (1993).
[4] B. I. Dunlap, Adv. Chem. Phys. **69**, 287 (1987).
[5] J. A. Pople, Angew. Chem., Int. Ed. **38**, 1895 (1999).
[6] K. S. Werpetinski and M. Cook, Phys. Rev. A **52**, R3397 (1995); J. Chem. Phys. **106**, 7124 (1997).
[7] J. C. Slater, Phys. Rev. **81**, 385 (1951).
[8] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[9] H. Sambe and R. H. Felton, J. Chem. Phys. **62**, 1122 (1975).
[10] B. G. Johnson, P. M. W. Gill, and J. A. Pople, J. Chem. Phys. **97**, 7846 (1992).
[11] B. I. Dunlap, J. W. D. Connolly, and J. R. Sabin, J. Chem. Phys. **71**, 3396 (1979); **71**, 4993 (1979).
[12] J. Andzelm and E. Wimmer, J. Chem. Phys. **96**, 1280 (1992).
[13] R. Fournier, J. Andzelm, and D. R. Salahub, J. Chem. Phys. **90**, 6371 (1989).
[14] B. I. Dunlap, J. Andzelm, and J. W. Mintmire, Phys. Rev. A **42**, 6354 (1990).
[15] A. Komornicki and G. Fitzgerald, J. Chem. Phys. **98**, 1398 (1993).
[16] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001).
[17] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).
[18] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[19] M. Petersilka, U. J. Gossmann, and E. K. U. Gross, Phys. Rev.

Lett. **76**, 1212 (1996).
[20] P. Pulay, J. Chem. Phys. **78**, 5043 (1983).
[21] B. I. Dunlap, Comput. Phys. Commun. **165**, 18 (2005).
[22] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
[23] X. Gonze, Phys. Rev. B **55**, 10337 (1997).
[24] B. I. Dunlap, J. Phys. Chem. A **107**, 10082 (2003).
[25] B. I. Dunlap, Phys. Rev. A **25**, 2847 (1982).
[26] B. I. Dunlap and S. P. Karna, in *Nonlinear Optical Materials*, edited by S. P. Karna and A. T. Yates, ACS Symposium Series No. 628 (ACS, Washington, DC, 1996), p. 164.
[27] G. D. Mahan, Phys. Rev. A **22**, 1780 (1980).
[28] P. Pulay, J. Comput. Chem. **3**, 556 (1982).
[29] R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics* (Academic, London, 1969), p. 129.
[30] P.-O. Löwdin, J. Mol. Spectrosc. **13**, 326 (1964).
[31] N. C. Handy, R. D. Amos, J. F. Gaw, J. E. Rice, and E. D. Simandiras, Chem. Phys. Lett. **120**, 151 (1985).
[32] N. C. Handy and H. F. Schaefer, J. Chem. Phys. **81**, 5031 (1984).
[33] B. I. Dunlap and W. N. Mei, J. Chem. Phys. **78**, 4997 (1983).
[34] R. K. Nesbet, Phys. Rev. A **56**, 2665 (1997).
[35] P. W. Ayers and W. Yang, J. Chem. Phys. **124**, 224108 (2006).
[36] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).
[37] A. D. Becke, J. Chem. Phys. **98**, 1372 (1993).
[38] N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, Can. J. Chem. **70**, 560 (1992).
[39] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys. **72**, 650 (1980).
[40] A. D. McLean and G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).
[41] K. Eichkorn, F. Weigend, O. Treutler, and R. Ahlrichs, Theor. Chem. Acc. **97**, 119 (1997).
[42] R. R. Zope and B. I. Dunlap, J. Chem. Theory Comput. **1**, 1193 (2005).
[43] R. R. Zope and B. I. Dunlap, Chem. Phys. Lett. **393**, 300 (2004).
[44] B. Champagne, E. A. Perpète, D. Jacquemin, S. J. A. van Gisbergen, E.-J. Baerends, C. Soubra-Ghaoui, K. A. Robins, and B. Kirtman, J. Phys. Chem. A **104**, 4755 (2000).