

Direct optimization method to study constrained systems within density-functional theory

Qin Wu and Troy Van Voorhis

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

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Consider a system with an arbitrary constraint on its electron density (e.g., that there are N charges on a certain group of atoms). We show that in Kohn-Sham density functional theory, the minimum energy state consistent with the constraint is actually a maximum with respect to the constraint potential, and that this solution is unique. This leads us to an efficient algorithm for calculations on constrained systems. Illustrative studies are shown for charge transfer in the zincbacteriochlorin-bacteriochlorin complex, polyene and alkane chains.

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Density functional theory (DFT) [1] is widely used in chemistry and solid-state physics to calculate various electronic ground-state properties. The normal procedure involves the energy minimization of a system with an external potential $v(\mathbf{r})$ by searching over all N -representable densities; that is

$$E_0 = \min_{\rho} \left(F[\rho] + \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \right). \quad (1)$$

It is important to note here that F , as a universal functional of ρ , is independent of $v(\mathbf{r})$. However, the above minimization does not locate any states other than the ground state of a given symmetry. It was later shown [2] that by making an appropriate choice of the external potential, one could use DFT to compute the lowest energy of a system with an arbitrary density constraint. The resulting constrained DFT (CDFT) formalism has been useful in describing charge [3] and magnetization [4] fluctuations in solids, predicting spin-dependent sticking of molecules on surfaces [5], parametrizing model Hamiltonians based on DFT calculations [6] and characterizing electron transfer reactions in molecules [7]. The CDFT approach to nonequilibrium systems should be thought of as a simplified version of time-dependent DFT (TDDFT) [8]. With TDDFT one can determine all the excited states of the system, whereas in CDFT one only has access to those states that are ground states of an alternative external potential. Now, to obtain the constrained state, one must first find the particular external potential that has the constrained state as its ground state. In previous applications, this has been accomplished by inspection; one scans over the potential and identifies the value that satisfies the desired constraint. This technique is computationally intensive and would be prohibitively difficult in a system with many independent constraints. In this paper, we provide a method that determines the constrained state directly. Our method, based on the previous work of calculating the exact Kohn-Sham (KS) potential from a given electron density [9], performs an unconstrained maximization to find the correct potential at each iteration in the self-consistent procedure. At convergence, it gives precisely the desired state and the required potential. We then demonstrate the efficiency of this method for a few electron transfer systems.

In the KS method [10], the electronic energy is written as

$$E[\rho] = \sum_{\sigma} \sum_i^{\alpha, \beta} \langle \phi_{i\sigma} | -\frac{1}{2} \nabla^2 | \phi_{i\sigma} \rangle + \int d\mathbf{r} v_n(\mathbf{r})\rho(\mathbf{r}) + J[\rho] + E_{xc}[\rho^{\alpha}, \rho^{\beta}], \quad (2)$$

where J is the classical Coulomb energy, E_{xc} is the exchange-correlation energy and v_n is the external potential. $N = \sum_{\sigma} N_{\sigma}$ is the total number of electrons and $\rho(\mathbf{r})$ is the electron density, $\rho(\mathbf{r}) = \rho^{\alpha} + \rho^{\beta} = \sum_{\sigma} \sum_i^{\alpha, \beta} |\phi_{i\sigma}(\mathbf{r})|^2$, with $\phi_{i\sigma}$ being the lowest energy orbitals for σ spin of the reference noninteracting system. Now add a general constraint to the density [2],

$$\sum_{\sigma} \int w_c^{\sigma}(\mathbf{r})\rho^{\sigma}(\mathbf{r})d\mathbf{r} = N_c, \quad (3)$$

where $w_c(\mathbf{r})$ acts as a weight function that defines the constrained property. For example, w_c could be 1 inside a domain C and 0 otherwise, thus constraining the number of electrons in C . To minimize the total energy in Eq. (2) under the constraint Eq. (3), a Lagrange multiplier, V_c , is used to build a functional

$$W[\rho, V_c] = E[\rho] + V_c \left(\sum_{\sigma} \int w_c^{\sigma}(\mathbf{r})\rho^{\sigma}(\mathbf{r})d\mathbf{r} - N_c \right). \quad (4)$$

Making W stationary under the condition that the orbitals are normalized gives the following equations:

$$\left(-\frac{1}{2} \nabla^2 + v_n(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc\sigma}(\mathbf{r}) + V_c w_c^{\sigma}(\mathbf{r}) \right) \phi_{i\sigma} = \varepsilon_{i\sigma} \phi_{i\sigma}, \quad (5)$$

with a similar one for $\phi_{i\sigma}^*$. These equations are the standard KS equations except for the addition of the constraint potential, $V_c w_c^{\sigma}(\mathbf{r})$, in the effective Hamiltonian. Although $w_c^{\sigma}(\mathbf{r})$ is predefined and known explicitly, V_c is only known implicitly: the correct V_c should make the density satisfy Eq. (3).

However, for any given V_c , Eq. (5) uniquely determines a set of orbitals. When these orbitals are used to calculate ρ and then W , W becomes a function of V_c only. This is the original idea behind optimized effective potential theory [11] and its generalization to potential functionals [12]. We now show that $W(V_c)$ is a strictly concave function of V_c following Ref. [9]. The first derivative of $W(V_c)$ is

$$\begin{aligned} \frac{dW}{dV_c} &= \sum_{\sigma} \sum_i \left(\frac{\delta W}{\delta \phi_{i\sigma}^*} \frac{\partial \phi_{i\sigma}^*}{\partial V_c} + \text{c.c.} \right) + \frac{\partial W}{\partial V_c} \\ &= \sum_{\sigma} \int w_c^{\sigma}(\mathbf{r}) \rho^{\sigma}(\mathbf{r}) d\mathbf{r} - N_c. \end{aligned} \quad (6)$$

Here the fact that $\delta W / \delta \phi_{i\sigma}^* = 0$, i.e., Eq. (5), has been used. The stationary point of $W(V_c)$ ($dW/dV_c = 0$) then restores the constraint Eq. (3) automatically. To determine the character of the stationary point, one needs to check the second derivative of $W(V_c)$,

$$\begin{aligned} \frac{d^2 W}{dV_c^2} &= \sum_{\sigma} \sum_i^{N_{\sigma}} \int w_c^{\sigma}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}) \frac{\delta \phi_{i\sigma}(\mathbf{r})}{\delta [V_c w_c^{\sigma}(\mathbf{r}')] } w_c^{\sigma}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \text{c.c.} \\ &= \sum_{\sigma} \sum_i^{N_{\sigma}} \int w_c^{\sigma}(\mathbf{r}) \phi_{i\sigma}^*(\mathbf{r}) \sum_{a \neq i} \frac{\phi_{a\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}')}{\epsilon_{i\sigma} - \epsilon_{a\sigma}} \phi_{a\sigma}(\mathbf{r}) \\ &\quad \times w_c^{\sigma}(\mathbf{r}') d\mathbf{r} d\mathbf{r}' + \text{c.c.} \\ &= 2 \sum_{\sigma} \sum_i^{N_{\sigma}} \sum_{a > N_{\sigma}} \frac{|\langle \phi_{i\sigma} | w_c^{\sigma} | \phi_{a\sigma} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{a\sigma}}. \end{aligned} \quad (7)$$

Here first-order perturbation theory is used to evaluate $\delta \phi_{i\sigma}(\mathbf{r}) / \delta [V_c w_c^{\sigma}(\mathbf{r}')]$. In the final expression, the index i goes over occupied orbitals, while a only has to go over the unoccupied orbitals because the summand is antisymmetric with the exchange of i and a . Assuming that the occupied orbitals are chosen as the lowest eigenstates, Eq. (7) is always nonpositive. This implies that there is only one stationary point and that it is a maximum. Thus by optimizing W through varying V_c , one can find the right V_c that produces the ground state of the constrained system. Because both first and second derivatives are easily calculated, the optimization can be done efficiently.

Like the KS equations, Eq. (5) must be solved in a self-consistent (SC) fashion because both the Coulomb potential and $v_{xc\sigma}(\mathbf{r})$ depend on ρ . At each SC iteration, a set of input $\phi_{i\sigma}$, either from an initial guess or from the output of previous iterations, is used to construct the conventional KS Hamiltonian. With an initial value of V_c , $V_c w_c^{\sigma}(\mathbf{r})$ is added to form the full Hamiltonian in Eq. (5). Then an optimization of V_c is carried out by repeating these steps, (i) solve Eq. (5); (ii) calculate the derivatives according to Eq. (6) and (7); and (iii) update V_c with an optimization scheme, such as Newton's method. The optimization of V_c is complete when the constraint, i.e., Eq. (3), is satisfied. The $\phi_{i\sigma}$ corresponding to the optimal V_c can be used as input for the next SC iteration. At convergence, this process yields both the ground state of the constrained system and the necessary potential to maintain the constraint.

In addition to the internal energy of the constrained system (E), one can also consider the "free energy," $G = E + V_c N_c$, which represents the energy of the system in the presence of the constraint. From the Hellmann-Feynman theorem, we have the thermodynamic relations

$$\frac{dE(N_c)}{dN_c} = -V_c \quad \text{and} \quad \frac{dG(V_c)}{dV_c} = N_c, \quad (8)$$

which reflect the fact that while E is a natural function of N_c , G is a natural function of V_c . One result of these relations is $d^2 E / dN_c^2 = -(d^2 W / dV_c^2)^{-1}$, which indicates that the concaveness of $W(V_c)$ is equivalent to the convexness of $E(N_c)$. The latter can be proven for a broader class of energy functionals [13].

Equation (3) can be used to enforce a variety of constraints, leading to various interesting applications. Instead of the total number of electrons in C , one can constrain the number of d or f electrons, which is important in studies of metal impurities [2] and superconductivity [6]. One can also constrain the difference between the number of α and β electrons on the same atom so as to study the change of local magnetic moments [14]. Alternatively, one can constrain the charge difference between two separated parts of the system, and this is useful to study charge transfer (CT) reactions [7]. In the present work, we focus on charge transfer. Therefore, there is an electron donor (D) in the system, which should give up electrons, and there is an electron acceptor (A), which should gain electrons. If N_D and N_A stand for the net charges on D and A , we then constrain the difference $N_c = (N_D - N_A) / 2$. This can be done in Eq. (3) by defining the weight function $w_c^{\sigma}(\mathbf{r})$ to be positive on the donor and negative on the acceptor.

We have implemented our method in NWChem [15]. There are, of course, many different ways of defining the charge on an atom within a molecule, and we have implemented five of them, Mulliken population, Löwdin population, atomic-orthogonalized Löwdin population [16], the real space weight function as suggested by Becke [17], and the Voronoi cell method [18]. We find that Mulliken populations can be qualitatively incorrect, often giving negative populations once the constraint is established. The other four methods all give similar results for systems discussed in this work. In what follows, we use Löwdin population.

As a first example, consider intermolecular charge transfer in the zincbacteriochlorin-bacteriochlorin (ZnBC-BC) complex (Fig. 1) [19]. There are two low-lying CT states, $\text{ZnBC}^+ \text{-BC}^-$ and $\text{ZnBC}^- \text{-BC}^+$. Linear response TDDFT calculations are known to give too low energies for these states [20]. Moreover, their potential energy curves as a function of the intermolecular distance, R , do not exhibit the correct $1/R$ dependence due to the lack of particle-hole interactions in the excited states [20]. We have used the same structure of (1,4)-phenylene-linked ZnBC-BC complex and the model complex as in Ref. [20].

For the model complex, we use our constraint formalism to calculate the energies of the lowest CT states at different distances between the separated subunits, starting from 5.84 Å as in the linked complex up to 9.0 Å. Energies are calculated using the Becke-Lee-Yang-Parr (BLYP) functional [21] and the 6-31G* basis set. The difference between the energy of the CT state and that of the ground state of the model complex at 5.84 Å shows an excellent linear relationship against the inverse of the distance [Fig. 2(a)] as it should. The last point of each line represents the CT state excitation

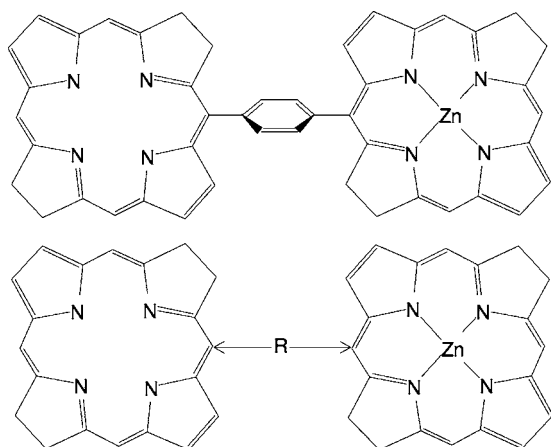


FIG. 1. Molecular structures of the linked zincbacteriochlorin-bacteriochlorin complex and the model complex. R refers to the distance between the two carbon atoms that are formerly linked.

energy of the model complex at the distance of the linked complex. These energies are 3.79 eV ($\text{ZnBC}^+-\text{BC}^-$) and 3.94 eV ($\text{ZnBC}^--\text{BC}^+$), comparing to 3.75 eV and 3.91 eV, respectively, as calculated by the hybrid method in Ref. [20]. The corresponding CT state excitation energies for the linked complex are 3.60 eV and 3.71 eV by the constrained DFT calculations, comparing to 1.32 eV and 1.46 eV calculated by TDDFT. Thus by doing only constrained ground-state DFT calculations, we are able to obtain a good picture of the lowest energy states of long-range charge transfer, which has been problematic for TDDFT. Our method can also be used to calculate states with partial charges, and therefore analyze the whole process of charge transfer. Examining the relation between the applied potential and the charge [Fig. 2(b)], we see two nearly parallel lines separated by a vertical jump at the zero charge point. As has been noticed previously [22], for two well-separated fragments, one expects a jump at zero charge that is nearly equal to the ionization potential (IP) of the electron donor minus the electron affinity (EA) of the acceptor, followed by two essentially horizontal lines. The

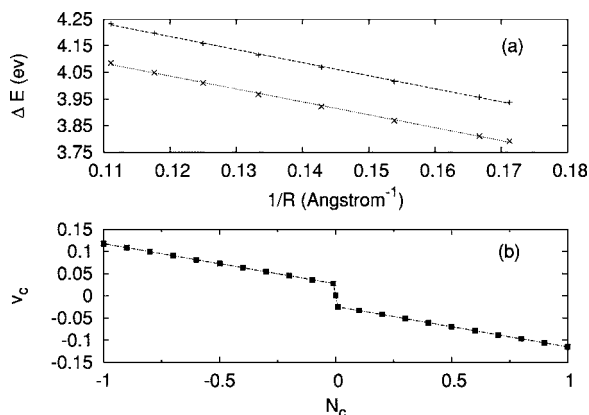


FIG. 2. (a) The lowest CT-state energies of the ZnBC-BC model complex at different distances as compared to its ground-state energy at 5.84 Å. Lower line, $\text{ZnBC}^+-\text{BC}^-$. Upper line, $\text{ZnBC}^--\text{BC}^+$. (b) Applied potential vs charge transfer for the model complex at 5.84 Å.

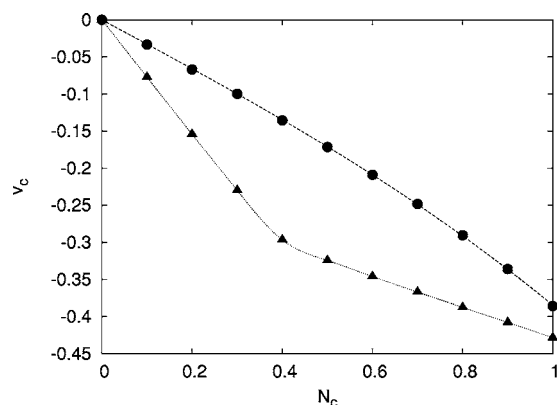


FIG. 3. Applied potential vs charge transfer for C_6H_8 (dots) and C_6H_{14} (triangles).

initial gap of BLYP is too small due to its lack of the derivative discontinuity in the exchange-correlation potential [22], and the ensuing slope of V_c versus N_c is too large because of the self-interaction error. However, the remarkable fact is that these two effects approximately cancel, giving an accurate energy at integer N_c .

Next we consider CT in polyenes (C_nH_{n+2}) and alkanes ($\text{C}_n\text{H}_{2n+2}$). The constraint is imposed on the end groups ($=\text{CH}_2$ for polyenes and $-\text{CH}_3$ for alkanes) and the charge is transferred from one end (donor) to the other (acceptor) in the molecule. All geometries are optimized with the B3LYP functional [23] and the 6-31G* basis set. The nuclear framework is then frozen for the subsequent CT calculations. Figure 3 shows the potential-charge curves for C_6H_8 and C_6H_{14} , where we see nearly linear response for C_6H_8 all the way to one charge transferred, but a significant deflection for C_6H_{14} .

To make sure that the deflection is not an error of DFT, we seek help from coupled-cluster (CC) methods [24]. For CC calculations, we do not have the same optimization procedure as in DFT to calculate V_c . Instead, we apply an external potential $V_c w_c^\sigma(\mathbf{r})$ explicitly and calculate the free energy of the perturbed system for various values of V_c . We then calculate N_c by finite difference according to Eq. (8). We have done singles and doubles coupled-cluster (CCSD) [25] calculations on $\text{C}_4\text{H}_9\text{F}$ [27,29], and compared the

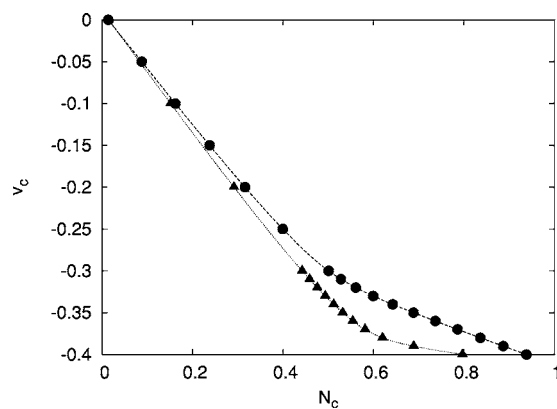


FIG. 4. Applied potential vs charge transfer for $\text{C}_4\text{H}_9\text{F}$. Dots, B3LYP. Triangles, CCSD.

potential-charge curve to B3LYP results as shown in Fig. 4. It is clear that the deflection remains, though in a different position from B3LYP results, and we therefore conclude that this is not an artifact of DFT. By plotting the density at various V_c values and monitoring the changes of the density between consecutive points, one can actually see a sudden change of the electron density, corresponding to the kink in the line. Further studies will be reported in later work [26].

Our method, implemented here with Gaussian basis functions for molecular systems, can also be generalized to extended systems using plane waves, as well as metallic systems where ensemble DFT is needed. For those cases, Eq. (7) is rewritten as

$$\frac{d^2W}{dV_c^2} = \sum_{\sigma} \int w_c^{\sigma}(\mathbf{r}) \frac{\delta \rho_{\sigma}(\mathbf{r})}{\delta [V_c w_c^{\sigma}(\mathbf{r}')] } w_c^{\sigma}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (9)$$

and techniques from density functional perturbation theory [28] can be employed.

In conclusion, we have presented an efficient DFT method to study constrained systems. This method directly optimizes the required potential to establish the constraint while solving the KS equations self-consistently. The charge transfer studies presented here demonstrate the efficacy of this approach and the wealth of information it provides. Future work will include extensions of this method to various aspects of charge and magnetization fluctuations, and analytic evaluation of the extra forces on atoms caused by the constrained potential. The forces are relatively easy to derive because of the variational nature of the method, and will allow constrained geometry optimizations and molecular dynamics.

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