

# A direct optimization method to study constrained systems within density functional theory

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Consider a system with an arbitrary constraint on its electron density (e.g. that there are  $N$  charges on an acceptor group). We show that 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 performing Kohn-Sham density functional theory calculations on constrained systems. Illustrative studies are shown for charge transfer in: the zincbacteriochlorin–bacteriochlorin complex, polyene and alkane chains, and stretched  $H_2$ .

In density functional theory (DFT) [1], the ground-state energy is obtained by the minimization:

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

where  $F[\rho]$  is a universal functional and  $v(\mathbf{r})$  is an external potential. The density at the minimum then is the ground-state density. The foundation laid down by Hohenberg, Kohn and Levy [1] guarantees the existence of  $F[\rho]$  and the validity of the minimization procedure. It is important to note that  $F[\rho]$  is independent of  $v(\mathbf{r})$ , and there are no restrictions on  $v(\mathbf{r})$ . 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 compatible 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], parameterizing model Hamiltonians based on DFT calculations [6] and characterizing electron transfer reaction in molecules [7]. The CDFT approach to non-equilibrium 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 letter, we provide a novel 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, 11], the electronic energy is written as: (We assume closed-shell systems and real orbitals for now, but it is straightforward to generalize the following scheme to other cases.)

$$E[\rho] = 2 \sum_i^{N/2} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle + \int d\mathbf{r} v_n(\mathbf{r})\rho(\mathbf{r}) + J[\rho] + E_{xc}[\rho], \quad (2)$$

where  $J$  is the classical Coulomb energy,  $E_{xc}$  is the exchange-correlation energy and  $v_n$  is the external potential.  $N$  is the number of electrons and  $\rho(\mathbf{r})$  is the electron density,  $\rho(\mathbf{r}) = 2 \sum_i^{N/2} \phi_i^2(\mathbf{r})$ , with  $\phi_i$  being the lowest energy orbitals of the reference noninteracting system. Now add a general constraint to the density:

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

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

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

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

$$\begin{aligned} [-\frac{1}{2} \nabla^2 + v_n(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}[\rho](\mathbf{r}) \\ + v_c w_c(\mathbf{r})] \phi_i = \varepsilon_i \phi_i. \end{aligned} \quad (5)$$

These equations are different from the KS equations because of the addition of the *constraint potential*,  $v_c w_c(\mathbf{r})$ , in the effective Hamiltonian. Unfortunately  $v_c$  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  $\rho$  and then  $W$ ,  $W$  becomes a function of  $v_c$  only. This is the original idea behind optimized effective potential

theory [12] and its generalization to potential functionals [13]. We now show that  $W(v_c)$  is a strictly concave function of  $v_c$  [9]. The first derivative of  $W(v_c)$  is

$$\frac{dW}{dv_c} = \sum_i \frac{\delta W}{\delta \phi_i} \frac{\delta \phi_i}{\delta v_c} + \frac{\partial W}{\partial v_c} = \int w_c(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} - N_c. \quad (6)$$

Here the fact that  $\delta W/\delta \phi_i = 0$ , 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  $W(v_c)$ ,

$$\begin{aligned} \frac{d^2 W}{dv_c^2} &= 4 \sum_i^{\text{occ}} \int w_c(\mathbf{r}) \phi(\mathbf{r}) \frac{\delta \phi_i(\mathbf{r})}{\delta [v_c w_c(\mathbf{r}')] } w_c(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= 4 \sum_i^{\text{occ}} \int w_c(\mathbf{r}) \phi(\mathbf{r}) \sum_{a \neq i} \frac{\phi_i(\mathbf{r}') \phi_a(\mathbf{r}')}{\varepsilon_i - \varepsilon_a} \phi_a(\mathbf{r}) \\ &\quad \times w_c(\mathbf{r}') d\mathbf{r} d\mathbf{r}' \\ &= 4 \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\langle \phi_i | w_c | \phi_a \rangle^2}{\varepsilon_i - \varepsilon_a} \end{aligned} \quad (7)$$

Here first-order perturbation theory is used to evaluate  $\frac{\delta \phi_i(\mathbf{r})}{\delta [v_c w_c(\mathbf{r}')]}$ . 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 non-positive. 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, Eqs. (5) have to be solved in a self-consistent (SC) fashion because both the Coulomb potential and  $v_{xc}$  depend on  $\rho$ . At each SC iteration, a set of input  $\phi_i$ , 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  $v_c$ ,  $v_c w_c(\mathbf{r})$  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  $\phi_i$  corresponding to the optimal  $v_c$  can be used as input for 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 ( $E[\rho]$ ), one can also consider the "free energy",  $F = E[\rho] + v_c N_c$ , which represents the energy of the system in the presence of the constraint. From the Hellmann-Feynman theorem, we have the thermodynamic relations

$$\frac{dE(N_c)}{dN_c} = -v_c \quad \text{and} \quad \frac{dF(v_c)}{dv_c} = \int w_c(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} = N_c, \quad (8)$$

which reflect the fact that while  $E$  is a natural function of  $N_c$ ,  $F$  is a natural function of  $v_c$ . From the variational principle, the internal energy of the constrained system is always higher than the unconstrained one, and the difference between these energies reflects the energy required to enforce the constraint.

Eq. (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 alpha and beta 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  $w_c(\mathbf{r})$  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 are often 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 analysis.

As a first example, consider intermolecular charge transfer in the zincbacteriochlorin-bacteriochlorin (ZnBC-BC) complex [19]. There are two low-lying CT states:  $\text{ZnBC}^+ \text{-BC}^-$  and  $\text{ZnBC}^- \text{-BC}^+$ . 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 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 a linear relationship against the inverse of the distance (Fig. 1a) as it should be. The last point of each line represents

the CT state excitation 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 as calculated by our method. 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. Of course, TDDFT also calculates the excited states higher in energy, while our method only gives the lowest energy state for a specific charge transfer. But 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. 1b), we see two nearly parallel lines separated by a vertical jump at the zero charge point. This is understandable because the two subunits of this complex are quite far from each other (5.84 Å). A sufficiently large force has to be applied to initiate the charge transfer from either one to the other. When the subunits are infinitely far apart, the magnitude of this force is the difference between the ionization potential (IP) of the electron donor and the electron affinity (EA) of the acceptor, and the graph in Fig. 1b will become two horizontal lines separated by a gap of  $(\text{IP}_{\text{ZnBC}} - \text{EA}_{\text{BC}}) + (\text{IP}_{\text{BC}} - \text{EA}_{\text{ZnBC}})$ . This is a clear manifestation of the derivative discontinuity of the exchange-correlation functional [22]. It is very difficult to account for these discontinuities in standard DFT, leading to a number of fundamental weakness (e.g., the “Band Gap Problem” [23]). It is therefore very encouraging that a constrained ground state is able to capture this elusive effect.

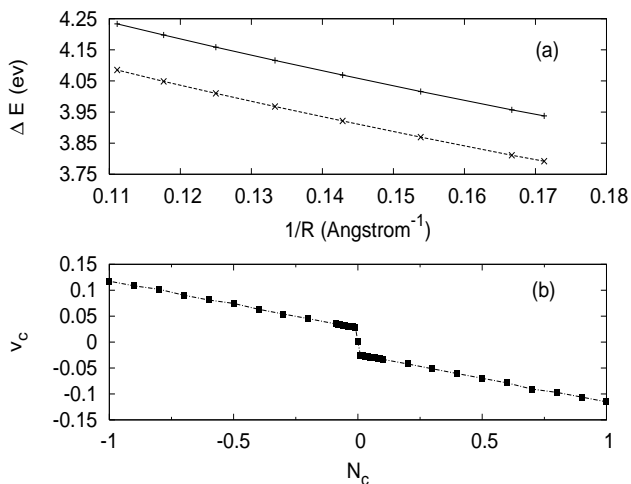


FIG. 1: (a) The lowest CT-state energies of the  $\text{ZnBC}-\text{BC}$  model complex at different distances as compared to its ground-state energy at 5.84 Å. Lower line:  $\text{ZnBC}^+-\text{BC}^-$ . Upper line:  $\text{ZnBC}^--\text{BC}^+$ . (b) Applied potential vs. charge transfer for the model complex at 5.84 Å.

Next we consider CT in polyenes ( $\text{C}_n\text{H}_{n+2}$ ) 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 [24] and the 6-31G\* basis set. Fig. 2 shows the potential-charge curves for  $\text{C}_6\text{H}_8$  and  $\text{C}_6\text{H}_{14}$ , where we see nearly linear response for  $\text{C}_6\text{H}_8$  all the way to one charge transferred, but a significant deflection for  $\text{C}_6\text{H}_{14}$ . This indicates that the polarizability of  $\text{C}_6\text{H}_8$  remains almost the same for the whole CT process, while that of  $\text{C}_6\text{H}_{14}$  changes abruptly upon increasingly applied potential. To make sure that the deflection is not an error of DFT, we seek help from coupled-cluster (CC) methods [25]. For CC calculations, we do not have the same optimization procedure as in DFT to calculate  $v_c$ . Instead, we apply an external potential  $v_c w_c(\mathbf{r})$  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) [26] calculations on  $\text{C}_4\text{H}_9\text{F}$  [29], and compared the potential-charge curve to B3LYP results as shown in Fig. 3. 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 on this point will be reported in later work [27].

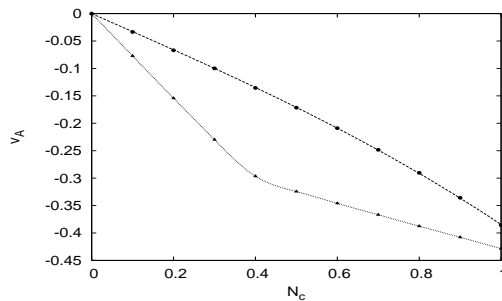


FIG. 2: Applied potential vs. charge transfer for  $\text{C}_6\text{H}_8$  (dots) and  $\text{C}_6\text{H}_{14}$  (triangles).

So far the systems have been closed-shell and the calculations have all been done with restricted KS (RKS). The results presented previously are not qualitatively altered by using an unrestricted KS (UKS) reference. As the last example, we pick a system that is known to be poorly described by RKS — the stretched singlet hydrogen molecule. We set the bond length between the two hydrogens as 3.5 Å. At such a distance, the true wavefunction has one electron on each atom. RKS has both electrons shared by both centers, which is clearly wrong. UKS is able to give the correct density picture, but suffers from spin contamination. For charge transfer between these two separated subunits, we expect to

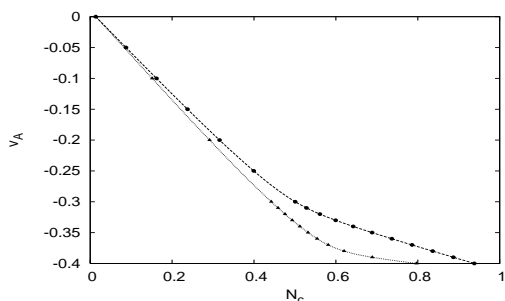


FIG. 3: Applied potential vs. charge transfer for  $C_4H_9F$ . Dots: B3LYP. Triangles: CCSD.

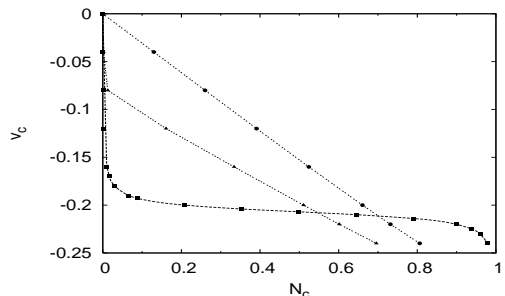


FIG. 4: Applied potential vs. charge transfer for stretched  $H_2$ . Circles: restricted B3LYP. Triangles: unrestricted B3LYP. Squares: CCSD.

see a picture similar to Fig. 1b; an initial barrier due to the energy gap between  $H^-$  and  $H^+$  must be overcome before charge transfer starts. This process is correctly described by CCSD calculations as seen in Fig. 4. The RKS results are clearly wrong. Charge transfer occurs even for a small bias and increases linearly with the applied potential. UKS calculations do have the initial barrier, which argues in favor of UKS for this case. However, compared to CCSD results, the barrier is too small, and the ensuing charge transfer acts in the same way as RKS. Hence, we conclude that existing functionals (restricted or unrestricted) are not sophisticated enough to deal with CT in diradical systems.

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. Extensions of this method to various aspects of charge and magnetization fluctuations should be equally fruitful.

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