

Constrained DFT for Charge Transfer Calculations and Predicting Polaron Conductivity in Battery Materials

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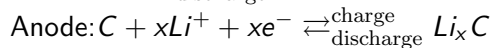
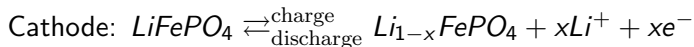
- 1 Charge transfer in battery materials
- 2 Charge Transfer Rates from DFT
- 3 Constrained DFT
- 4 Testing cDFT
- 5 Towards more conductive battery materials
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Table of Contents

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- 2 Charge Transfer Rates from DFT
- 3 Constrained DFT
- 4 Testing cDFT
- 5 Towards more conductive battery materials
- 6 Conclusions

Charge transfer in batteries

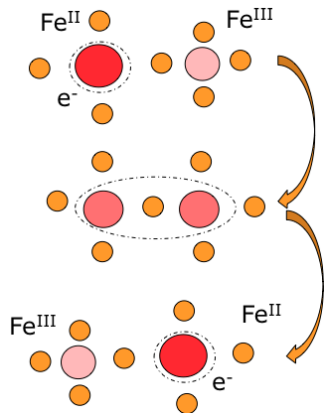
- The general operating mechanism is based on redox reactions and ion and electron transfer between the anode and cathode



- While the anode is usually a good electric conductor, the cathode is usually an oxide with a (large) band gap
- Charge transfer at the cathode is one the limiting factors in fast charging and discharging

Polaronic conduction

- The cathode materials are either insulators or semiconductors
- In the bulk, holes/electrons are conducted by consecutive hops from a redox centre to another - the polaronic mechanism
- The actual mechanism depends on the material but the charge transfer can be adiabatic or diabatic



Our goal is to computationally screen and find materials with improved bulk conductivity. Need a model for charge transfer...

Table of Contents

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- 4 Testing cDFT
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- 6 Conclusions

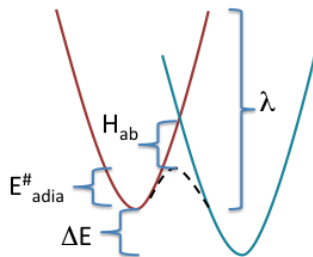
The Marcus model

- The Marcus model is the most common picture for electron transfer
- Built with two valence band/diabatic states to form a 2x2 Hamiltonian

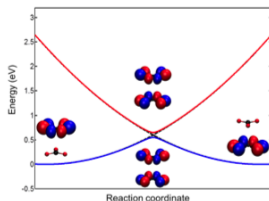
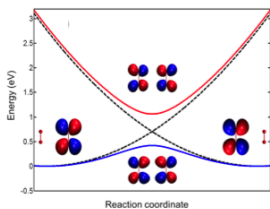
$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}$$

- with $H_{AB} = \langle \Psi_A | \hat{H} | \Psi_B \rangle$
- The adiabatic can be recovered by solving

$$\mathbf{Hc} = E\mathbf{Sc}$$



The Marcus Equation



$$k_{ad} = v_{eff} \exp \left[-\frac{E_{\ddagger ad}}{k_b T} \right]$$

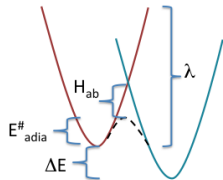
$$k_{nonad} = \frac{2\pi}{\hbar} \frac{H_{ab}}{\sqrt{4\pi\lambda k_b T}} v_{eff} \exp \left[-\frac{E_{\ddagger nonad}}{k_b T} \right]$$

- To capture both the adiabatic and non-adiabatic cases we use the Landau-Zener version of Marcus equation

$$k = \kappa_{el} \Gamma_{tun} v_{eff} \exp \left[-\frac{E_{\ddagger nonad} + \Delta E}{k_b T} \right]$$

Parametrising the Marcus equation

- The coupling constant $H_{ab} = \langle \Psi_a | \hat{H} | \Psi_b \rangle$
- Reorganisation energy $\lambda =$ Energy of the initial state at the final state geometry. An *excited state property*
- Adiabatic transition state energy in terms of ΔE , λ , and H_{ab}
- Marcus theory needs diabatic, charge-localised states which are very difficult to obtain with standard DFT



To calculate λ and H_{ab} and to obtain diabatic/localised state we have implemented constrained DFT in GPAW

Table of Contents

- 1 Charge transfer in battery materials
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- 3 Constrained DFT**
- 4 Testing cDFT
- 5 Towards more conductive battery materials
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cDFT basics

- cDFT is an external potential to KS equations which forces predefined atoms to carry a specified charge or magnetisation
- The cDFT energy is formally a constrained DFT energy

$$F[n(\mathbf{r}), V_c] = E^{KS}[n] + \sum_i V_i \sum_{\sigma} \left(\int d\mathbf{r} w_i^{\sigma}(\mathbf{r}) n^{\sigma}(\mathbf{r}) - N_i \right)$$

- This also gives rise to *spin-dependent external potential*

$$v_{eff}^{\sigma} = \frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})} = \frac{\delta E^{KS}[n(\mathbf{r})]}{\delta n(\mathbf{r})} + \sum_i V_i w_i^{\sigma}(\mathbf{r})$$

- The KS equations with this new potentials are solved self-consistently to determine V_i which yields

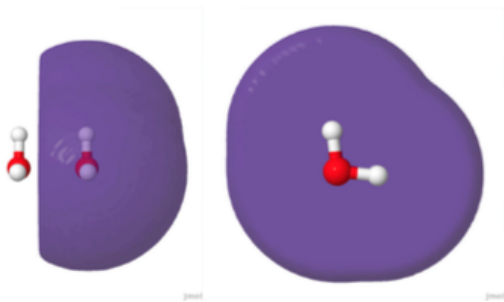
$$C \geq \left| \sum_{i,\sigma} \int d\mathbf{r} w_i^{\sigma}(\mathbf{r}) n^{\sigma}(\mathbf{r}) - N_i \right|$$

The weight function

- We use a real-space Hirshfeld charge partition with Gaussians

$$w_i(\mathbf{r}) = \frac{\sum_{j \in i} \rho_j(\mathbf{r})}{\sum_k \rho_k(\mathbf{r})}$$

$$\rho_i(\mathbf{r}, \mathbf{R}_i) = \frac{N_{el,i}}{\sigma_i \sqrt{2\pi}} \exp \left\{ -\frac{(\mathbf{r} - \mathbf{R}_i)^2}{2\sigma_i^2} \right\}$$



Updating the Lagrangian

- To have a fully self-consistent cDFT, the Lagrangian needs to be determined
- For this a two-stage optimisation is carried out

$$F[V_c] = \min_n \max_{\{V_c\}} \left[E^{KS}[n(\mathbf{r})] + \sum_i V_i \left(\int d\mathbf{r} w_i(\mathbf{r}) n(\mathbf{r}) - N_i \right) \right]$$

- The inner optimisation requires that the energy is stationary wrt to V_i . For this the derivative is

$$\frac{dF}{dV_i} = \int d\mathbf{r} w_i(\mathbf{r}) n(\mathbf{r}) - N_i = 0$$

- We use the SciPy `optimize.minimize` to carry out the inner optimization which gives access to many different methods

cDFT forces

- As a new potential is added, the forces need to be updated

$$\begin{aligned} f_A &= -\nabla_A F = -\nabla_A E^{KS} - \sum_i V_c \nabla_A \int d\mathbf{r} n(\mathbf{r}) w_c(\mathbf{r}) \\ &= f_A^{KS} + f_A^{cDFT} \end{aligned}$$

$$f_A^{cDFT} = -V_c \int d\mathbf{r} n(\mathbf{r}) \frac{\partial w_c(\mathbf{r}, \mathbf{R})}{\partial R_A}$$

cDFT with PAW

- Instead of using the all-electron densities, we use the pseudo density and an atomic correction for the density

$$F[n(\mathbf{r}), V_c] = E^{KS}[n(\mathbf{r})] + \sum_i V_i \left(\int d\mathbf{r} w_i(\mathbf{r}) \tilde{n}(\mathbf{r}) + \sum_{a \in i} \int_{\Omega_a} d\mathbf{r} w_i(\mathbf{r}) \Delta n^a(\mathbf{r}) - N_i \right)$$

$$\Delta n^a(\mathbf{r}) = \sum_{i,j} \sqrt{4\pi} D_{ij}^a Y_{00} \left[\phi_j^{a*}(\mathbf{r}) \phi_i^a(\mathbf{r}) - \tilde{\phi}_j^{a*}(\mathbf{r}) \tilde{\phi}_i^a(\mathbf{r}) \right]$$

$$+ \sqrt{4\pi} Y_{00} \left[-Z^a \delta(r) + n_c^a(\mathbf{r}) - \tilde{n}_c^a(\mathbf{r}) \right]$$

$$+ Z^a$$

- The same splitting is used whenever density is needed

cDFT with PAW

- We also need the PAW-cDFT Hamiltonian

$$\hat{H} = V_i w_i^\sigma + h_{atomic}^\sigma$$

$$h_{atomic}^\sigma = V_i \int_{a \in i} d\mathbf{r} w_i^\sigma(\mathbf{r}) \sum_a \sum_{i,j} \left[\phi_i^a \phi_j^a - \tilde{\phi}_i^a \tilde{\phi}_j^a \right] f_n^\sigma |\tilde{p}_i^a\rangle \langle \tilde{p}_j^a|$$

- ... and forces

$$\begin{aligned} f_A^{cDFT} &= - \left. \frac{dF[n(\mathbf{r}, V_c)]}{dR_A} \right|_{|\tilde{\psi}_n\rangle} \\ &= \sum_i \left[-V_c \int d\mathbf{r} \tilde{n}(\mathbf{r}) \frac{\partial w_c(\mathbf{r}, \mathbf{R})}{\partial R_A} \right. \\ &\quad \left. - \sum_{i,j} \int_{A \in c} d\mathbf{r} V_c w_c(\mathbf{r}) \Delta O_{ij}^a \frac{\partial D_{ij}^a}{\partial R_A} \right] \end{aligned}$$

Parametrising Marcus theory with cDFT

- Need to calculate λ and H_{ab} and to obtain diabatic/localised state
 - λ is easily computed with cDFT as the energy difference of the final state geometry using the constraint of the initial state and the initial state energy
 - cDFT states are both diabatic and localised
 - The coupling term $H_{AB} = \langle \psi_A | H_B^{KS} | \psi_B \rangle = G_B S_{AB} - V_B W_{AB}$
 - $G_A = \langle \psi_A | H_A^{KS} + \sum_i V_i^A w_i | \psi_A \rangle$, $S_{AB} = \langle \psi_A | \psi_B \rangle$ and $W_{AB} = \langle \psi_A | \sum_i w_i^B(\mathbf{r}) | \psi_B \rangle$

Parametrising Marcus theory with GPAW-cDFT

- To compute W_{AB} and S_{AB} , the wave-function are expanded as Slater determinants with *all-electron orbitals*

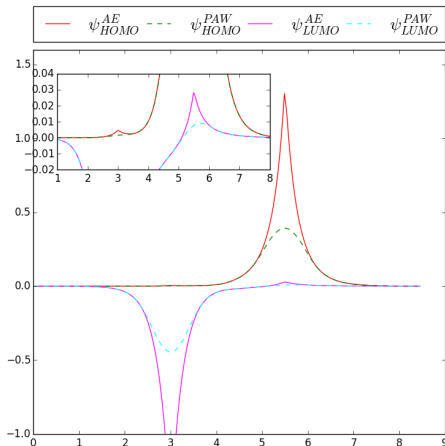
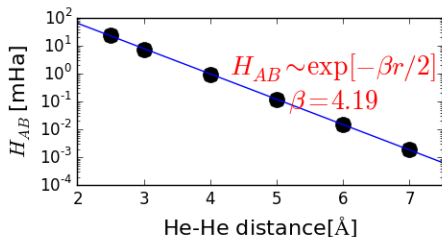
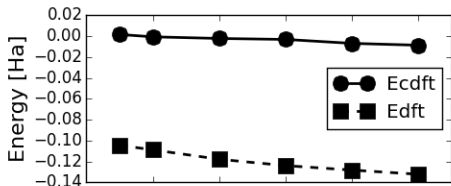


Table of Contents

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$(\text{He}_2)^+$ dissociation and coupling

- Despite its seeming simplicity, $(\text{He}_2)^+$ dissociation is very difficult for DFT
- Due to self-interaction error, a delocalised-state is favoured by DFT whereas a charge-localisation should take place
- cDFT has the correct behaviour with the energy ≈ 0 and localised charge
- The coupling constants agree well with other methods and cDFT implementations

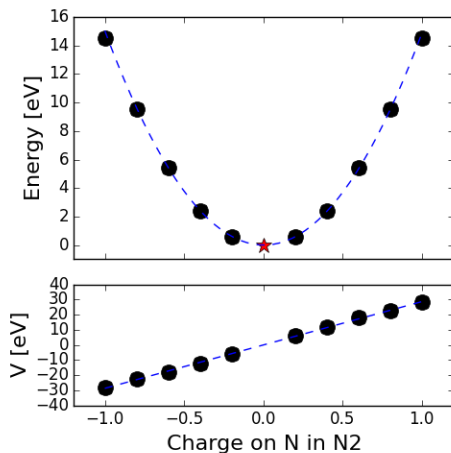


$(\text{Zn}_2)^+$ coupling

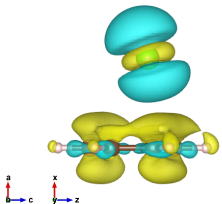
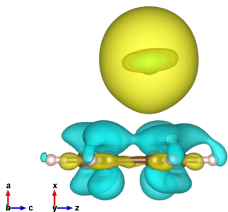
Table: Comparison of coupling constants in Zn_2^+ as a function of distance from different cDFT implementations and weight functions to high-level GMH data. Becke, Löwdin and Hirschfeld refer to different weight function definitions used in cDFT. β is the exponential decay constant.

	r [Å]					
	5	6	7	8	9	β
Becke	5.87	1.52	0.400	0.105	0.026	2.70
Löwdin	15.0	6.51	2.29	0.537	0.101	2.50
Hirschfeld						2.66
GMH	7.26	2.16	0.623	0.171	0.044	2.55
This work	16.71	4.83	1.35	0.39	0.11	2.51

Charge re-organisation in N_2



- cDFT gives the correct DFT energy for unconstrained systems

Charge transfer in (benzene-Cl)⁻

Method	H_{ab}
CDFT-CPMD	55.9
FO	17.2
CDFT-NWchem	48.8
GMH	51.0
This work	65.1

Table of Contents

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- 3 Constrained DFT
- 4 Testing cDFT
- 5 Towards more conductive battery materials**
- 6 Conclusions

Polarons from cDFT

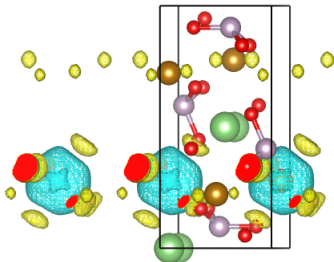


Figure: Charge difference unconstrained DFT and cDFT for hole in LiFePO_4^+ showing charge localisation on an iron atom. The light blue mesh corresponds to positive charge accumulation and the yellow to charge depletion.

Conductivity from cDFT and Marcus theory

- Using cDFT we can extract the parameters for Marcus theory and compute the charge transfer rate
- The conductivity as a function of potential/electric field (\mathbf{F}) can be calculated from the stationary master equation

$$\frac{\partial p_a}{\partial t} = \sum_a [k_{a \rightarrow b} p_a (1 - p_b) - k_{b \rightarrow a} p_b (1 - p_a)] = 0$$

$$\sigma = \frac{\sum_{ab} k_{a \rightarrow b} p_a (1 - p_b) R_{ab,F}}{\sum_a p_a |\mathbf{F}|}$$

$$R_{ab,F} = \frac{\mathbf{R}_{ab} \cdot \mathbf{F}}{|\mathbf{F}|}$$

- We also take into account how the rate changes with the electric field

Screening for cathode materials with improved conductivity

- The long-term goal is to use computations to screen for new cathode materials
- Use cDFT to parametrise Marcus theory for charge / polaron transfer rates to be used for solving the conductivity with the master equation
- Study effects of doping etc. on the conductivity
- Hopefully come up with new materials to study experimentally

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To conclude

- We are building a way to screen for more conductive battery materials
- Charge transfer rates from Marcus theory which is parametrised with cDFT implemented in GPAW
- Conductivities using the master equation with charge transfer rates for polaronic transport