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Electrostatic Mean-field and Degenerate Density Functional Perturbation Theories for Electrochemistry

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14. ABSTRACT Electrochemical systems are comprised of large collections of interacting particles in a complex environment. Therefore, they can often be well described by a continuum distribution of particles interacting in the local mean field. Density functional theory, on the other hand, typically describes smaller systems of a few hundred atoms but uses an expression for the electron-electron interaction energy that behaves similarly to electrochemical mean field theory. In fact, a link exists between the perturbation theory associated with both of these methods. In this work, we develop a perturbation theory and method to solve for equilibrium distributions of electrochemical systems and extend density functional perturbation theory in electrochemically relevant ways.						
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EXECUTIVE SUMMARY

This work develops the connection between electrochemical mean-field perturbation theory and degenerate density functional perturbation theory. Because electrochemical charge transfer as described by Marcus theory occurs between degenerate states [1, 2], it also extends density functional perturbation theory to the electrochemically relevant case of time-dependent perturbations in degenerate systems.

Two computational codes were developed over the course of this project. The first performs density-functional perturbation calculations and interfaces with an existing density functional code developed at NRL by Dr. Brett Dunlap. The second computes equilibrium distributions of interacting chemical species between charged capacitor plates.

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ELECTROSTATIC MEAN-FIELD AND DEGENERATE DENSITY FUNCTIONAL PERTURBATION THEORIES FOR ELECTROCHEMISTRY

1. INTRODUCTION

Hermann Von Helmholtz showed in 1853 that a double layer of ions forms along the boundary of an electrode submerged in an ionic solution. The inner layer is made up of ions with the opposite charge of the electrodes, attracted by electrostatic forces, and the outer layer is made up of ions with the same charge as the electrode, repelled from the electrode but attracted by the first layer. Together, the two layers form a dielectric that stores electrostatic charge.

A more detailed description of ion distribution was provided independently by Louis George Gouy and Leonard Guy Chapman, who developed a model where the ions behave obey the diffusion equation while interacting in the mean local electrostatic field. The ionic distributions in this model obey the Poisson-Boltzmann equation, so that the electrostatic energy of the charge distribution follows Boltzmann statistics [3].

Such descriptions, where particles interact with some mean field generated by the surrounding particles, are known as mean-field theories. Mean-field theories are useful not only in electrochemistry, but also in electronic structure theory to describe electron-electron interactions. The original derivation of Hartree-Fock was as a mean-field theory, and the Coulomb potential that it utilizes is the average electrostatic potential of the electrons.

The Kohn-Sham (KS) [4] formulation of density functional theory (DFT) [5] models electron-electron interaction energy as a nonlinear functional of the electron density $E_{ks}(\rho)$. This functional is separated into two parts: the Coulomb energy, which is the potential energy of a classical charge distribution, ρ , and the exchange-correlation energy, which contains the remainder of the interaction energy. Although the exact form of the exchange-correlation energy is unknown, several good approximations exist in the form of local and semi-local functionals, which depend only on the local electron-density and its gradient.

Minimizing the energy in KS DFT results in a set of KS equations that describe single-particle non-interacting orbitals, which can be used to (approximately) reproduce the exact, interacting electron density. Because the Coulomb and exchange-correlation energies are nonlinear functions of the electron density, the KS equations have the form of nonlinear mean-field equations.

Electrochemical mean-field theory and DFT are, in this way, closely linked. In fact, as we develop the perturbation theory electrochemical mean-field theory, we will see that it has the same form as DFT perturbation theory. In both cases, a first-order density is found by solving an implicit equation, which involves inverting a matrix that depends on either the variation of the Coulomb plus exchange-correlation potential or the chemical potential with respect to a density.

Furthermore, just as the electron-electron interaction energy can be separated into a Coulomb term, which can be exactly expressed as a functional of electron-density, and the less precisely understood exchange-correlation energy, a similar separation can be made in the chemical potential. Because the form of the chemical potential of an ideal solution is known, it can be separated from the portion of the chemical potential that must be approximated, and which contains the interactions of the system.

This work develops the perturbation theory for electrochemical mean-field theory. Because first-order perturbation theory represents the first-derivative of some property of the system with respect to some perturbing potential, we demonstrate that it can be numerically integrated to obtain an exact solution for the equilibrium concentration of chemical species in an electrochemical environment.

We also extend our prior work on degenerate DFT perturbation theory to the time dependent case. According to Marcus theory, electron-transfer occurs when there is a degeneracy between electronic states. Therefore, we expect that degenerate DFT perturbation theory is important for describing electron-transfer processes. It is hoped that the development of both mean-field and DFT perturbation theory will inform future models of electrochemistry that merge the two together.

2. ELECTROCHEMICAL MEAN-FIELD PERTURBATION THEORY

We start with a solution composed of multiple ionic species with different electrochemical properties such as charge and polarizability. According to the diffusion equation, the current of chemical species i with concentration $C_i(\mathbf{r})$ is related to the gradient of its electrochemical potential, $\tilde{\mu}_i(\mathbf{r})$, by

$$\mathbf{J}_i(\mathbf{r}) = DC_i(\mathbf{r}) \frac{\nabla \tilde{\mu}_i(\mathbf{r})}{RT}, \quad (1)$$

where D is the diffusion constant, T is the temperature. and R is the gas constant, and we have made the assumption that D is constant throughout space.

In the limit of non-interacting ions at low concentration, $\tilde{\mu}_i$ becomes $RT \ln C_i(\mathbf{r})$. We can therefore, separate this “free” or “non-interacting” portion of the electrochemical potential from the remainder, which we call $\bar{\mu}_i(\mathbf{r})$. With this definition, $\bar{\mu}_i$ is given by

$$\bar{\mu}_i(\mathbf{r}) = \frac{\delta(U - W_{ext})}{\delta C_i(\mathbf{r})} - RT \ln(C_i(\mathbf{r})). \quad (2)$$

Here, U is the total energy of the system, which can be computed to an arbitrary level of theory, and W_{ext} any external work done on the system by, for example, a voltage source. The potential $\bar{\mu}_i$, then, is analogous to the exchange-correlation potential of density functional theory, in that it is a black box which contains everything not described by an ideal, non-interacting system.

Equilibrium occurs when the current is zero everywhere, corresponding to a constant electrochemical potential. Setting $\mathbf{J}_i(\mathbf{r})$ equal to zero, we get

$$0 = \frac{D}{RT} C_i(\mathbf{r}) \nabla [\bar{\mu}_i(\mathbf{r}) + RT \ln(C_i(\mathbf{r}))] = D \left[C_i(\mathbf{r}) \frac{\nabla \bar{\mu}_i(\mathbf{r})}{RT} + \nabla C_i(\mathbf{r}) \right], \quad (3)$$

which has the solution

$$C_i(\mathbf{r}) = C_{0i} e^{-\bar{\mu}_i(\mathbf{r})/RT}. \quad (4)$$

Obtaining the actual form of Eq. (4) as a function of \mathbf{r} is deceptively complicated because $\bar{\mu}_i(\mathbf{r})$ is a function not only of $C_i(\mathbf{r})$, but of all other $C_j(\mathbf{r}')$ as well. A computationally tractable solution can be obtained by scaling some or all of the interactions by a coupling constant, λ , and gradually increasing it from zero to one. Let us further split $\bar{\mu}_i$ into

$$\bar{\mu}_i(\mathbf{r}) = \bar{\mu}_i^0(\mathbf{r}) + \lambda \bar{\mu}_i'(\mathbf{r}), \quad (5)$$

where $\bar{\mu}_i^0(\mathbf{r})$ is a potential an interaction for which we know the equilibrium concentration and $\bar{\mu}_i'(\mathbf{r})$ represents the potential of some more complicated interaction. The potential $\bar{\mu}_i'(\mathbf{r})$ need not be small, and it even suffices to set $\bar{\mu}_i = 0$ so that all interactions are contained within $\bar{\mu}'(\mathbf{r})$.

In neutral solutions, where the equilibrium concentrations in the absence of an external potential are uniform, it suffices to adiabatically turn on external interactions. For systems with a non-zero net charge, where the equilibrium concentrations are unknown, we can still start from uniform concentrations if all interactions are turned on adiabatically.

While the former method has some advantages, such as the ability to generate an adiabatic current density when a field is gradually turned on, we shall present only the latter method because it is not limited to neutral systems. Both methods use essentially the same framework, and is not difficult to infer the changes when only some, rather than all, interactions are scaled by λ .

To preserve the normalization of each $C_i(\mathbf{r})$ as $\bar{\mu}$ changes, we divide by a denominator that keeps the integral of $C_i(\mathbf{r}, \lambda)$ fixed and write

$$C_i(\mathbf{r}, \lambda) = C_{0i} \frac{e^{-\lambda \bar{\mu}_i(\mathbf{r}, \lambda)/RT}}{\int e^{-\lambda \bar{\mu}_i(\mathbf{r}', \lambda)/RT} d\mathbf{r}'}, \quad (6)$$

which has the solution $C_i(\mathbf{r}) = C_{0i}$ at $\lambda = 0$. We can find $C_i(\mathbf{r}, \lambda + \Delta\lambda)$ from $C_i(\mathbf{r}, \lambda)$ by using the Taylor series

$$C_i(\mathbf{r}, \lambda + \Delta\lambda) = C_i(\mathbf{r}, \lambda) + \frac{\partial C_i(\mathbf{r}, \lambda)}{\partial \lambda} \Delta\lambda + \frac{1}{2} \frac{\partial^2 C_i(\mathbf{r}, \lambda)}{\partial \lambda^2} \Delta\lambda^2 + \dots \quad (7)$$

Because $\bar{\mu}_i$ is a function of every C_j , its Taylor series in λ looks like

$$\bar{\mu}_i(\mathbf{r}, \lambda + \Delta\lambda) = \bar{\mu}_i(\mathbf{r}) + \bar{\mu}_i'(\mathbf{r}) \Delta\lambda + \sum_j \left[\frac{\delta \bar{\mu}_i^0(\mathbf{r})}{\delta C_j(\mathbf{r}, \lambda)} \Delta\lambda + \lambda \frac{\delta \bar{\mu}_i'(\mathbf{r})}{\delta C_j(\mathbf{r}, \lambda)} \right] \frac{\partial C_j(\mathbf{r}, \lambda)}{\partial \lambda} \Delta\lambda + \dots, \quad (8)$$

where, for compactness, we have omitted the argument λ from $\bar{\mu}_i$ when $\Delta\lambda$ is zero.

In the language of perturbation theory, the Nth term in the Taylor series is the Nth-order term in the perturbation series for $C_i(\mathbf{r})$. To first order, we get

$$\frac{\partial C_i(\mathbf{r})}{\partial \lambda} = -C_{0i} \frac{\frac{\delta \bar{\mu}_i(\mathbf{r})}{\delta \lambda} e^{-\bar{\mu}_i(\mathbf{r})/RT}}{RT \int e^{-\lambda \bar{\mu}_i(\mathbf{r}')/RT} d\mathbf{r}'} + C_{0i} \frac{e^{-\lambda \bar{\mu}_i(\mathbf{r})/RT} \int \frac{\delta \bar{\mu}_i(\mathbf{r}')}{\delta \lambda} e^{-\lambda \bar{\mu}_i(\mathbf{r}')/RT} d\mathbf{r}'}{RT \left(\int e^{-\lambda \bar{\mu}_i(\mathbf{r}'')/RT} d\mathbf{r}'' \right)^2}, \quad (9)$$

where, from Eq. (8),

$$\frac{\delta \bar{\mu}_i(\mathbf{r})}{\delta \lambda} = \bar{\mu}'_i(\mathbf{r}) + \int d\mathbf{r}' \sum_j \left[\frac{\delta \bar{\mu}_i^0(\mathbf{r})}{\delta C_j(\mathbf{r}')} + \lambda \frac{\delta \bar{\mu}'_i(\mathbf{r})}{\delta C(\mathbf{r}')} \right] \frac{\partial C_j(\mathbf{r}')}{\partial \lambda}. \quad (10)$$

Using the definition of $C_i(\mathbf{r})$ from Eq. (6), Eq. (9) can be solved and rewritten as

$$\begin{aligned} \frac{\partial C_i(\mathbf{r})}{\partial \lambda} = \sum_j \int d\mathbf{r}' \left[\delta(\mathbf{r} - \mathbf{r}') \delta_{ij} \left(1 + \bar{\mu}'_i(\mathbf{r}) - \frac{C_i(\mathbf{r})}{C_{0i}} \int d\mathbf{r}'' \mu'(\mathbf{r}'') C_i(\mathbf{r}'') \right) + \left(\frac{\delta \bar{\mu}_i^0(\mathbf{r})}{\delta C_j(\mathbf{r}')} + \lambda \frac{\delta \bar{\mu}'_i(\mathbf{r})}{\delta C_j(\mathbf{r}')} \right) C_i(\mathbf{r}) \right. \\ \left. - \frac{C_i(\mathbf{r})}{C_{0i}} \int d\mathbf{r}'' \left(\frac{\delta \bar{\mu}_i^0(\mathbf{r}'')}{\delta C_j(\mathbf{r}')} + \lambda \frac{\delta \bar{\mu}'_i(\mathbf{r}'')}{\delta C_j(\mathbf{r}')} \right) C_i(\mathbf{r}'') \right]^{-1} C_j(\mathbf{r}') \end{aligned} \quad (11)$$

where the inverse is a matrix inverse. If \mathbf{r} and \mathbf{r}' are discretized over a finite set of points, then the pairs \mathbf{r}, i and \mathbf{r}', j can be combined to form the two matrix indices.

This defines a differential equation which can be integrated as

$$C_i(\mathbf{r}, 1) = \int_0^1 \frac{\partial C_i(r)}{\partial \lambda} d\lambda \quad (12)$$

to find the concentration of fully interacting particles, starting from an easily computed distribution of non-interacting particles.

2.1 The interactions of charged, polarizable particles

So far, we have described a completely general method for finding equilibrium concentrations of interacting chemical species that is independent of the form interaction. In this section, we will apply the theory a solution composed of two chemical species with charges q_i and polarizability α_i .

We give our system planar symmetry, so that the solution is contained in a box of length L with electrodes at either end that we treat as infinite planes. The electrodes are connected to an external voltage source that holds the potential between them at V by adjusting their charge. The charge on plate at L is given by Q_{AB} .

There are any number of ways that we could use our perturbation theory to turn on interactions in the system. We could, for example 1) start with an initial solution where our particles interact with the external field of the capacitor plates but not with each other, and gradually turn on the interaction between particles,

or 2) start with neutral particles and gradually turn on their interactions both with each other and with the external field, or 3) start with neutral capacitor plates and gradually turn on their charge.

While we have been able to achieve a numerical solution using all three of the methods above, we will develop the equations to implement to the third method here. The modifications required for either of the other two methods are straightforward. In the third method, the charge on the capacitor plates is scaled by λ , where at $\lambda = 0$ the plates are neutral and at $\lambda = 1$, the potential across the plates is held at V . Because the distribution of the two chemical species changes as λ goes from zero to one, Q_{AB} changes in a nonlinear manner.

Between the electrodes, the electric field at point x is given by

$$E(x) = \sum_i E_i(x) - \frac{V}{L}, \quad (13)$$

where $E_i(x)$ is the electric field produced by one particular chemical species.

The gradient of the electric field in this one-dimensional system, from Maxwell's equations is

$$\frac{\partial}{\partial x} E(x) = \frac{1}{\epsilon} \sum_i \left[q_i C_i(x) - \alpha_i \frac{\partial}{\partial x} (E(x) C_i(x)) \right], \quad (14)$$

where the second term on the right-hand side is the polarization charge, equal to the gradient of the local polarization for each chemical species, which is equal to $\alpha_i C_i E(x)$. We can rearrange this equation to get

$$\frac{\partial}{\partial x} \left(1 + \sum_i \frac{\alpha_i}{\epsilon} C_i(x) \right) E(x) = \frac{1}{\epsilon} \sum_i q_i C_i(x). \quad (15)$$

Solving for $E(x)$, we get

$$E(x) = \frac{q_i \int_0^x C_i(x') dx' - \int_x^L C_i(x') dx'}{2\epsilon \left(1 + \frac{1}{\epsilon} \sum_j \alpha_j C_j(x) \right)} - \frac{V}{L}. \quad (16)$$

The final term, V/L comes from the electric field of the capacitor plates and is a boundary condition on the differential equation in Eq. (15).

The interacting portion of the chemical potential, $\bar{\mu}_i(\mathbf{r})$, as we defined it in the previous section, is given by the variation of the total interaction energy minus the work done by an external source, with respect to the concentration of chemical species i . The total interaction energy is simply the energy stored in the electric field plus the dielectric strain energy of the polarized species,

$$U = \frac{\epsilon}{2} \int_0^L E(x)^2 dx - \sum_i \frac{\alpha_i}{2} \int_0^L E^2(x) C_i(x) dx. \quad (17)$$

The external work is provided can be obtained from the energy stored in the capacitor, $Q_{AB}V$, and is provided by the external voltage source. If the charge on the capacitor plates is changed to keep the voltage constant, it must satisfy the equation

$$\frac{Q_{AB}}{\epsilon}L - \sum_i \int_0^L E_i(x)dx = V. \quad (18)$$

If we scale the charge by λ , so that it can be gradually turned on, we get

$$Q_{AB} = \lambda \frac{\epsilon}{L} \left(V + \sum_i \int_0^L E_i(x)dx \right), \quad (19)$$

and the external work done by the voltage source in response to changing $C_i(x)$ is

$$\delta W = \lambda \delta Q_{AB}V = V \sum_i \int dx \frac{\delta Q_{AB}}{\delta C_i(x)} \delta C_i(x) = \lambda \frac{\epsilon}{L} \sum_{ij} \int_0^L dx' \frac{\delta E_j(x')}{\delta C_i(x)} \delta C_i(x). \quad (20)$$

With that, we can now calculate the chemical potential as

$$\bar{\mu}_i(x) = \frac{\delta}{\delta C_i(x)} \frac{\delta(U-W)}{\delta C_i(x)} = -\frac{1}{2} \alpha_i E(x)^2 + \int_0^L \left(\epsilon - \frac{\epsilon}{\lambda} - \sum_j \alpha_j C_j(x') \right) E(x') \frac{\delta E(x')}{\delta C_i(x)} dx' \quad (21)$$

with

$$\frac{\delta E_j(x)}{\delta C_i(x')} = \frac{1}{\epsilon} \frac{1}{1 + \frac{1}{\epsilon} \sum_k \alpha_k C_k(x)} \left(\frac{x-x'}{|x-x'|} \frac{q_i \delta_{ij}}{2} - \alpha_i E_j(x) \delta(x-x') \right). \quad (22)$$

For our system with only two chemical species, we can write

$$\sum_j \frac{\delta E_j(x)}{\delta C_i(x)} = \frac{1}{2\epsilon} \left(\frac{1}{1 + \frac{\alpha_1}{\epsilon} C_1(x) + \frac{\alpha_2}{\epsilon} C_2(x)} \right)^2 \left[Q_i + \frac{1}{\epsilon} (q_1 \alpha_1 - q_2 \alpha_2) C_2(x') \right] \frac{x-x'}{|x-x'|}. \quad (23)$$

Our equations also require $\delta \bar{\mu}_i(x) / \delta C_j(x')$, which is given by

$$\begin{aligned} \frac{\delta^2(U-W)}{\delta C_i(x) \delta C_j(x')} &= -\alpha_i \frac{\delta E(x)}{\delta C_j(x')} E(x) - \alpha_j \frac{\delta E(x')}{\delta C_i(x)} E(x') + \int_0^L dx'' \left(\epsilon - \frac{\epsilon}{L} - \sum_k \alpha_k C_k(x'') \right) \\ &\quad \times \left(\frac{\delta E(x'')}{\delta C_j(x')} \frac{\delta E(x'')}{\delta C_i(x)} + E(x'') \frac{\delta^2 E(x'')}{\delta C_i(x) \delta C_j(x')} \right), \end{aligned} \quad (24)$$

and, for our system,

$$\sum_k \frac{\delta^2 E_k(x)}{\delta C_i(x') \delta C_j(x'')} = \delta(x' - x'') \frac{1}{2\epsilon} \left(\frac{1}{1 + \frac{\alpha_1}{\epsilon} C_1(x) + \frac{\alpha_2}{\epsilon} C_2(x)} \right)^3 \left[-\alpha_1 q_2 - \alpha_2 q_1 + \frac{\alpha_1 \alpha_2 q_1 - \alpha_1^2 q_2}{\epsilon} C_1(x') + \frac{\alpha_1 \alpha_2 q_2 - \alpha_1^2 q_1}{\epsilon} C_2(x') \right] \frac{x - x'}{|x - x'|}. \quad (25)$$

The delta function, $\delta(x' - x'')$ is convenient from a numerical standpoint, because storage of this term only requires a two-index tensor (matrix), rather than a three-index tensor.

2.2 Demonstration of method

A code for electrochemical mean-field perturbation theory was developed in Matlab. It calculates the first-order change in the local density of chemical species as chemical interactions are turned on. This first-order change corresponds to the first-derivative of concentration with respect to the strength of the interactions. The differential equation resulting from this first-derivative is plugged into Matlab's ordinary differential equation solver to find the equilibrium density of each chemical species as a function of position.

The code uses planar symmetry, assuming two planar electrodes, each held at a fixed potential, with a solution containing two chemical species between them. The chemical species are allowed to have properties of charge and polarizability. In planar symmetry, unlike in spherical or cylindrical symmetry, charged particles can interact with charges both to the left and to the right, and therefore the solution to the problem of interacting charges in this environment is non-trivial. Increasing the polarizability of the two species beyond physically reasonable values, increasing their concentration, and giving them both positive charges all increased the amount of time it took to integrate over λ , but for most parameters, we were eventually able to find a solution.

Here, we have plotted the results for a simple test case with a two-component solution composed of equal amounts of positive and negative ions with ± 1 electron on each. The initial concentrations were set to be a uniform 0.01 mol/liter (10 mol/m³) and a potential of 1 V was perturbatively turned on across the two plates. Plate separations of both 1 and 10 μm were used, with 1000 grid points in both cases.

The concentration of positive ions drops off nearly to zero in the span of a few nanometers from the negative electrode, and the negative ions do likewise at the positive electrode. increasing the plate separations beyond 10 μm only results in a larger region of zero concentration and requires a larger number of grid points to capture the fine detail near the edges.

Because the concentration drops off so quickly, it is better visualized on a logarithmic plot than a linear plot. However, the term we have dubbed the "ideal" chemical potential is proportional to the log of the concentration, and in Fig. 1, we have plotted the ideal, interaction, and total chemical potentials of the positive ions for both plate separations. The total chemical potential is constant, as required by the condition that there is no ion-current. The plots for the negative ions are identical, but flipped across the horizontal axis.

In Fig. 2, the electrostatic potential is plotted between the two plates. Although the negative and positive ions largely shield the electric field of the two plates, at this concentration, they cannot shield it completely. The residual electric field causes the electrostatic potential to increase nearly linearly once the concentration of ions in the solution becomes negligible. This is most apparent at the larger plate separation, where the nonlinear effects are confined to a proportionally smaller region.

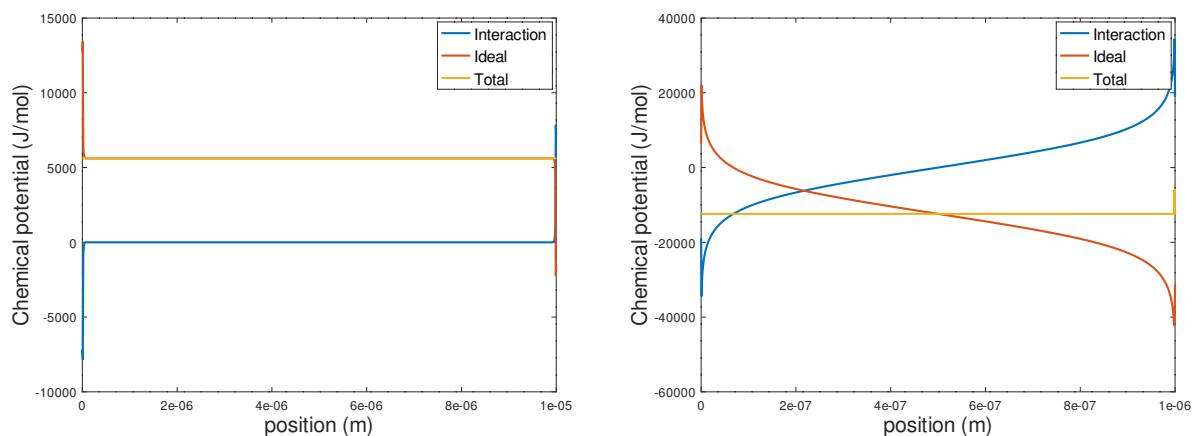


Fig. 1 — Components of the chemical potential of the positive ions between plates $10\ \mu\text{m}$ (left) and $1\ \mu\text{m}$ (right) apart. The chemical potential is broken into an “ideal” component (natural log of the concentration) and an “interaction” portion, which is the remainder. The total chemical potential is constant between the plates.

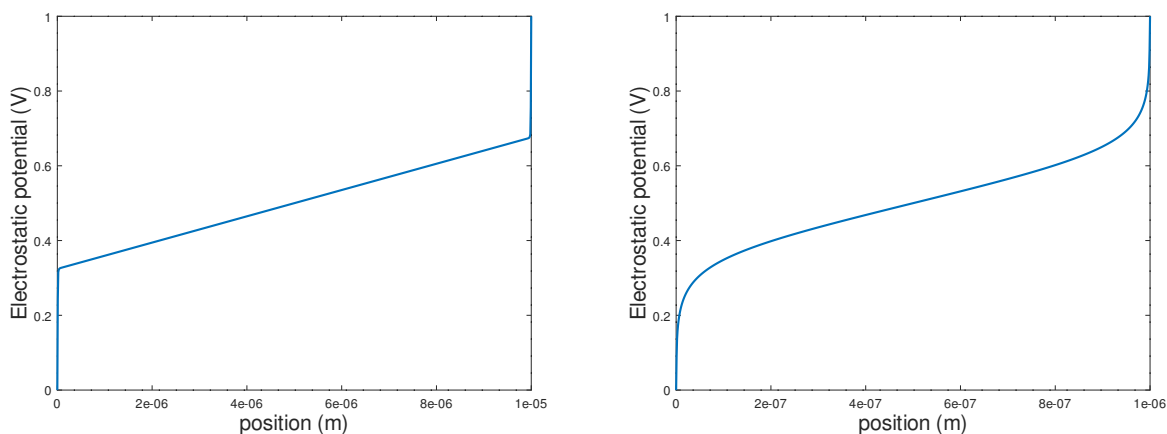


Fig. 2 — Electrostatic potential between plates $10^{-2}\ \text{mm}$ (left) and $10^{-3}\ \text{mm}$ (right) apart

2.3 Summary of electrochemical mean-field perturbation theory

We have developed a perturbation theory for electrochemical mean-field theory that treats the chemical potential much like the exchange-correlation potential of density functional theory. The “ideal” portion of the potential, proportional to the natural log of the concentration, is separated from the remainder, which must be modeled with some appropriate approximation. Approximating the remainder by the electrostatic interaction of polarizable point charges results in equilibrium concentrations similar to those predicted by Poisson-Boltzmann. However, our integrated perturbative approach allows for the governing equations to be solved in more complex environments, and potentially, for the utilization of more sophisticated approximations to the interaction potential.

A potential improvement to this algorithm could be made by taking another lesson from quantum chemistry and use a linear combination of basis functions to represent the ion concentrations. This could take the form of an adaptive grid, with more points near the plates and fewer near the center, plane waves, for periodic systems, or possibly Gaussians, for three-dimensional non-periodic system.

3. OCCUPATION NUMBERS IN TIME-DEPENDENT DFT PERTURBATION THEORY

Time-dependent density functional theory (TDDFT) was first formalized in 1984 by Runge and Gross [6]. The Runge-Gross theorems eventually lead to the time-dependent KS equations and linear response TDDFT [7], which has proven to be an invaluable tool for calculating electronic excitation energies. The equations for linear response result from first-order perturbation theory applied to the electron density, which is taken to be a sum over non-interacting KS orbitals squared. These orbitals evolve in time according to the time-dependent KS equation, and typically contain either one or zero electrons, initially filled in the order of their eigenvalues.

However, this procedure for filling orbitals is not always sufficient to generate a ground state. In certain degenerate KS systems, the ground state electron density can only be achieved with fractionally occupied orbitals at the Fermi-level, so that the density, ρ , is given by

$$\rho(\mathbf{r}) = \sum_i n_i \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}), \quad (26)$$

where ϕ_i is a molecular orbital and $0 \leq n_i \leq 1$. Examples of such a system include both the Fe_6Al_8 cluster and atomic iron [8] computed with Slater exchange [9] and VWN correlation [10]. In the latter system, the ground state consists of fractionally occupied degenerate $3d$ and $4s$ orbitals [8, 11].

If a particular N -electron density can be produced by integer occupation of the lowest N eigenstates of some local potential, it is known as noninteracting v -representable. Noninteracting v -representability was explored early on by Levy, who showed the existence of reasonable-looking densities that cannot be reproduced by the ground state of a noninteracting potential [12]. Later empirical tests of v -representability have confirmed the existence interacting systems with ground states that are not noninteracting pure-state v -representable. Schipper found that multiconfiguration densities for C_2 could only be reproduced with fractional occupation numbers in the KS system [13]. Similarly, Morrison [14], who obtained KS potentials from a Levy constrained search procedure, found that the interacting ground states of the Be isoelectric series were not pure-state v -representable in the noninteracting system. Katriel, who first demonstrated noninteracting v -representability for all densities in a four dimensional Hilbert space [15], later found non-degenerate two-particle interacting systems with densities that do not correspond to the ground state of any local one-body potential [16].

Importantly, these studies show that a lack of noninteracting v -representability does not imply degeneracy in the interacting system. This is also implied by the behavior of KS DFT itself. It was shown by Ullrich and Kohn in 2002 [17] that every noninteracting potential with a degenerate ground state is embedded in a manifold of potentials which also have degenerate ground states. More recently, developments in DFT perturbation theory have shown that when any small perturbing potential is applied to a degenerate state, the orbital occupation numbers change in response so that the Coulomb and exchange-correlation potentials adjust themselves to preserve the degeneracy of the system [11, 18, 19]. By contrast, in the real, interacting

system, almost any perturbing potential will break its degeneracy. Therefore, there cannot be a one-to-one correspondence between degenerate KS and interacting systems.

The mismatch between degeneracy in the KS and interacting systems is not precluded by Janak’s theorem [20], which implies only that the first derivative of energy is zero as electrons are moved between degenerate orbitals. Second and higher derivatives in general need not be zero.

Herein lies the problem in current formulations of KS TDDFT. The adiabatic theorem (which can be extended to degenerate states [21], even perturbatively, as we will also demonstrate) implies that a slow perturbation should cause a system to remain in its ground state at any given time. Therefore, KS TDDFT must include a mechanism for occupation numbers to evolve in time when degeneracy is present. If not, then the system cannot time-evolve into the ground state of certain potentials or remain in the ground state if a perturbation is applied to a degenerate state. In other words, it would imply that certain ground states can never be achieved in practice.

While density-matrix functional theory allows for time-dependent occupation numbers [22, 23], which is largely responsible for its success in describing molecular dissociation [24], current formulations of KS TDDFT do not. In this paper, we develop equations to govern the non-adiabatic time dependence of fractionally occupied, degenerate orbitals by requiring that they reduce to time-independent perturbation theory in the appropriate limit.

In Section 3.1, we provide justification for the claim that time-dependent perturbation theory should reduce to time-independent perturbation theory in the adiabatic limit, even for degenerate states. We demonstrate that this is the case, up to a time-dependent phase factor, in standard quantum mechanics. We show that the first-order mixing between degenerate states, which arises from a second-order expansion of the Schrödinger equation in time-independent perturbation theory, instead arises as part of an infinite sum in time-dependent perturbation theory.

In Section 3.2, we demonstrate that the trivial extension of TDDFT to include fractional occupation numbers does not automatically result in their time-dependence. In Section 3.1, we show how the equations for occupation numbers can be solved in time-independent perturbation theory. Then, in Section 3.4, we look at the linear response of both the interacting density and the KS orbitals, and from there, propose an frequency-dependent extension of the first-order equations for occupation numbers. In Section 3.5, we apply our equations to atomic iron and find excitation energies that correspond to changes in occupation numbers. summarizing comments follow.

3.1 Time-dependent degenerate perturbations in the adiabatic limit

Expressions for the adiabatic time-evolution of a system typically involve energy differences in the denominator, which become singular in the presence of degeneracy. Therefore, some justification must be provided that the adiabatic theorem still applies to degenerate states. Furthermore, it is not clear that the adiabatic theorem necessarily applies order-by-order in perturbation theory. Here, we will demonstrate that both in the degenerate and non-degenerate case, first-order time-dependent perturbation theory reduces to first-order time-independent perturbation theory in the adiabatic limit. Because we have not yet fully defined time-dependent degenerate perturbation theory in KS DFT, we will show that this holds for standard quantum mechanical perturbation theory.

At first-order, time-independent degenerate perturbation theory says that

$$|\Psi_i^{(1)}\rangle = \sum_j |\Psi_j\rangle \frac{\langle\Psi_j|V^{(1)}|\Psi_i\rangle}{E_i - E_j} + \sum_{jk} \frac{|\Psi_k\rangle \langle\Psi_k|V^{(1)}|\Psi_j\rangle \langle\Psi_j|V^{(1)}|\Psi_i\rangle}{(\langle\Psi_i|V^{(1)}|\Psi_i\rangle - \langle\Psi_k|V^{(1)}|\Psi_k\rangle)(E_i - E_j)}, \quad (27)$$

where Ψ_i and Ψ_k are degenerate eigenstates and j is summed only over non-degenerate states. Of particular interest is the second term, which mixes degenerate states into one another. Although it contains two powers of $V^{(1)}$ in the numerator, it is first-order because it contains a power of $V^{(1)}$ in the denominator as well. A similar term arises in DFT [19], although it does not affect the first-order density.

Although this term is first-order, it shows up in the second-order expansion of the time-independent Schrödinger equation. Similarly, we will show how this arises as a hidden first-order term in time-dependent perturbation theory as the first-order part of an infinite sum of terms from all orders.

We begin by considering a Hamiltonian that contains a zeroth-order time-independent component and a time-dependent perturbation

$$H(t) = H^{(0)} + V^{(1)}(t). \quad (28)$$

Rather than using the interaction picture as is often done, let us simply expand the propagator, \mathbf{U} , in terms of λ as

$$\mathbf{U} = \mathbf{U}^{(0)} + \lambda \mathbf{U}^{(1)} + \lambda^2 \mathbf{U}^{(2)} + \dots, \quad (29)$$

where $\mathbf{U}^{(0)}$ is the propagator of the unperturbed system, $\exp(-iH^{(0)}t)$.

We can take the matrix elements of the Schrödinger equation associated with this propagator between two eigenstates Ψ_k and Ψ_i

$$\partial_t \langle\Psi_k|\mathbf{U}|\Psi_i\rangle = -i\langle\Psi_k|H(t)\mathbf{U}|\Psi_i\rangle, \quad (30)$$

and pull out the first-order component on both sides to get

$$\partial_t \langle\Psi_k|\mathbf{U}^{(1)}|\Psi_i\rangle = -i\langle\Psi_k|V^{(1)}(t)|\Psi_i\rangle e^{-iE_i t} - iE_k \langle\Psi_k|\mathbf{U}^{(1)}|\Psi_i\rangle \quad (31)$$

This is a first-order differential equation which has a particular solution and a complimentary solution

$$(\partial_t + iE_k) \langle\Psi_k|\mathbf{U}^{(1)}|\Psi_i\rangle_p = -i\langle\Psi_k|V^{(1)}(t)|\Psi_i\rangle e^{-iE_i t} (\partial_t + iE_k) \langle\Psi_k|\mathbf{U}^{(1)}|\Psi_i\rangle_c = 0. \quad (32)$$

We will show how the first-order matrix elements of the propagator reduce to time-independent perturbation theory for the degenerate case and non-degenerate case separately. We will begin with the non-degenerate case, where this is simpler.

3.1.1 The non-degenerate case

When the matrix elements we are interested in are between non-degenerate eigenstates, to find the particular solution, we Fourier transform \mathbf{U} and $V^{(1)}(t)$ to get

$$-i \int (\omega' - E_k) \langle \Psi_k | \mathbf{U}^{(1)}(\omega') | \Psi_i \rangle_p e^{-i\omega' t} d\omega' = -i \int \langle \Psi_k | V^{(1)}(\omega) | \Psi_i \rangle e^{-i(\omega + E_i)t} d\omega. \quad (33)$$

For both sides to be equal, we must equate identical frequency components, which happens when $\omega' = \omega + E_i$. Therefore,

$$-i(\omega + E_i - E_k) \langle \Psi_k | \mathbf{U}^{(1)}(\omega + E_i) | \Psi_i \rangle_p = -i \langle \Psi_k | V^{(1)}(\omega) | \Psi_i \rangle, \quad (34)$$

which gives us the usual term used for developing linear response

$$\langle \Psi_k | \mathbf{U}^{(1)} | \Psi_i \rangle_p = \int \frac{\langle \Psi_k | V^{(1)}(\omega) | \Psi_i \rangle}{\omega + E_i - E_k} e^{-i(\omega + E_i)t} d\omega, \quad (35)$$

and this reduces to time-independent perturbation theory with an additional phase if ω goes to zero.

The complementary solution,

$$\langle \Psi_k | \mathbf{U}^{(1)} | \Psi_i \rangle_c = C_{ik} e^{-iE_k t}, \quad (36)$$

can be used to match boundary conditions so that $\mathbf{U}^{(1)}$ is zero at some t_0 for a perturbation that is switched on at a particular time.

3.1.2 The degenerate case

If E_i and E_k are equal, Eq. (34) gives us

$$\omega \langle \Psi_k | \mathbf{U}^{(1)}(\omega + E_i) | \Psi_i \rangle_p = \langle \Psi_k | V^{(1)}(\omega) | \Psi_i \rangle, \quad (37)$$

which either means that the matrix elements of $V^{(1)}$ must be zero in the adiabatic limit, or the matrix elements of $\mathbf{U}^{(1)}$ become infinite. There are two reasons for this. First, unlike in the nondegenerate case, an arbitrary basis of degenerate eigenstates is not adiabatically connected to a set of perturbed eigenstates. Second, the first-order term, which grows linearly in time between degenerate states, converges to an exponential at higher orders. To explore both of these things in more detail, we will change from the frequency domain back into the time domain.

We will assume that we have an time-independent perturbation turned on adiabatically by

$$V^{(1)}(t) = \lim_{\alpha \rightarrow 0} e^{\alpha t} V^{(1)}. \quad (38)$$

The complementary solution for the propagator, which is used to match the boundary condition that $\mathbf{U} = \mathbf{U}^{(0)}$ at $t = -\infty$ and constant at any finite time is simply

$$\langle \Psi_k | \mathbf{U} | \Psi_i \rangle_c = 0. \quad (39)$$

To find the particular solution, note that at any finite time $\exp(\alpha t) = 1$, $V^{(1)}$ is time-independent, and we can choose a new basis of degenerate Ψ_k that diagonalizes $V^{(1)}$. The equation for the first-order propagator for degenerate Ψ_k and Ψ_i then becomes

$$(\partial_t + iE_k) \langle \Psi_k | \mathbf{U}^{(1)} | \Psi_i \rangle_p = -i\delta_{ik} \langle \Psi_i | V^{(1)} | \Psi_i \rangle e^{-iE_i t}, \quad (40)$$

from which, because $E_k = E_i$, it follows that

$$\langle \Psi_k | \mathbf{U}^{(1)} | \Psi_i \rangle_p = -i\delta_{ik} \langle \Psi_i | V^{(1)} | \Psi_i \rangle t e^{-iE_i t}. \quad (41)$$

For matrix elements where Ψ_k is outside of the degenerate space, we get the same solution as Eq. (35) with $\omega = 0$.

We can continue on to second-order to get

$$(\partial_t + iE_k) \langle \Psi_k | \mathbf{U}^{(2)} | \Psi_i \rangle_p = -i \langle \Psi_k | V^{(1)} \sum_j | \Psi_j \rangle \langle \Psi_j | \mathbf{U}^{(1)} | \Psi_i \rangle. \quad (42)$$

If we separate out the degenerate and nondegenerate Ψ_j in the summation, we get

$$(\partial_t + iE_k) \langle \Psi_k | \mathbf{U}^{(2)} | \Psi_i \rangle_p = -\langle \Psi_k | V^{(1)} | \Psi_i \rangle \langle \Psi_i | V^{(1)} | \Psi_i \rangle t e^{-iE_i t} - i \langle \Psi_k | V^{(1)} \sum_j | \Psi_j \rangle \langle \Psi_j | \frac{V^{(1)}}{E_i - E_j} | \Psi_i \rangle t e^{-iE_i t}, \quad (43)$$

where the sum is now only over non-degenerate orbitals.

At N th-order, our equation for $\mathbf{U}^{(N)}$ becomes

$$(\partial_t + E_k) \langle \Psi_k | \mathbf{U}^{(N)} | \Psi_k \rangle_p = -i \langle \Psi_k | V^{(1)} \mathbf{U}^{(N-1)} | \Psi_k \rangle_p, \quad (44)$$

and it is obvious that if we continue to infinite order considering only matrix elements between degenerate eigenstates, we will get a series that sums to

$$\sum_{N=0}^{\infty} \frac{1}{N!} \left(-i \langle \Psi_i | V^{(1)} | \Psi_i \rangle t \right)^N e^{-iE_i t} = e^{-i(V_{ii} + E_i)t}, \quad (45)$$

where we have employed the shorthand $V_{ji} = \langle \Psi_j | V^{(1)} | \Psi_i \rangle$. We will continue to use this shorthand for a time for its compactness, but we will put our final equations back in our original notation.

We can also look at the terms like the second one in Eq. (43) that leave the degenerate space and return, and sum every term that includes exactly one copy of $V_{kj}V_{ji}$, where j is outside the degenerate space, and i and k are in the degenerate space. These terms have N diagonal elements V_{ii} to the right, followed by $V_{kj}V_{ji}$, followed M diagonal elements V_{kk} to the left. To start, our sum from Eq. (45) and continue on to the next order by adding a V_{ji} term to get the equation

$$(\partial_t + E_j) \langle \Psi_j | \mathbf{U}^{(s)} | \Psi_i \rangle_p = -iV_{ji}e^{-i(V_{ii}+E_i)t}, \quad (46)$$

which has the solution

$$\langle \Psi_j | \mathbf{U}^{(s)} | \Psi_i \rangle_p = \frac{V_{ji}e^{-i(V_{ii}+E_i)t}}{V_{ii} + E_i - E_j}. \quad (47)$$

Now, to the left of this, we must add V_{kj} followed by M copies of V_{kk} summed over $M = 1$ to infinity, and solve the appropriate differential equation at each order. Because E_k is degenerate with E_i , the energy differences $E_k - E_i$ will vanish from our differential equations, and our solution looks like

$$\begin{aligned} \sum_{M=0}^{\infty} \int (-iV_{kk})^M \left(\frac{V_{kj}V_{ji}e^{-iV_{ii}t}}{V_{ii}(V_{ii} + E_i - E_j)} \right) dt^M e^{-iE_i t} &= \frac{V_{kj}V_{ji}e^{-i(V_{ii}+E_i)t}}{V_{ii}(V_{ii} + E_i - E_j)} \sum_{M=0}^{\infty} \left(\frac{V_{kk}}{V_{ii}} \right)^M \\ &= \frac{V_{kj}V_{ji}e^{-i(V_{ii}+E_i)t}}{(V_{ii} - V_{kk})(V_{ii} + E_i - E_j)}. \end{aligned} \quad (48)$$

This expression is a mix of terms from all orders of perturbation theory, but we can pull from it a first-order term. We do this by making the substitution $V^{(1)} \rightarrow \lambda V^{(1)}$, expanding Eq. (48) as a Taylor series in λ , and pulling out only the terms proportional to a single power of λ . Doing so, and switching back to our original notation, we get

$$\frac{\langle \Psi_k | V^{(1)} | \Psi_j \rangle \langle \Psi_j | V^{(1)} | \Psi_i \rangle e^{-iE_i t}}{(\langle \Psi_i | V^{(1)} | \Psi_i \rangle - \langle \Psi_k | V^{(1)} | \Psi_k \rangle) (E_i - E_j)}, \quad (49)$$

which matches exactly the result from time-independent perturbation theory, with an additional time-dependent phase factor.

3.2 Indifference of the action to occupation numbers

As we mentioned earlier, the fact that the ground states of different potentials have different occupation numbers implies that there must be some way for occupation numbers to change under a time-dependent potential. The obvious extension of time-dependent KS DFT fails to capture this, however, as we will illustrate below. To begin, let us write the energy in time-independent DFT with fractional occupation numbers:

$$E = \sum_i n_i \langle \phi_i | -\frac{1}{2} \nabla^2 + V_{ext}(\mathbf{r}) | \phi_i \rangle + E_{ks}[\rho], \quad (50)$$

where $E_{ks}[\rho]$ is the Coulomb plus exchange-correlation (XC) energy as a functional of ρ . The most straightforward way to define the action for TDDFT with fractional occupation numbers is then,

$$\mathcal{S} = \int_0^t \sum_i n_i \langle \phi_i | -\frac{1}{2} \nabla^2 + V_{ext} + i \partial_t | \phi_i \rangle + E_{ks}[\rho] dt. \quad (51)$$

While varying the action with respect to ϕ_i^* is straight forward, one might suspect through naive application of the Euler-Lagrange formula that a term proportional to dn_i/dt arises when varying \mathcal{S} with respect to ϕ_i . However, some care must be taken so as not to neglect non-vanishing surface terms when integrating by parts. Doing so, we get

$$\mathcal{S} = \int_0^t \left[\sum_i n_i \langle \phi_i | -\frac{1}{2} \nabla^2 + V_{ext} | \phi_i \rangle + E_{ks}[\rho] \right] + \sum_i i [n_i]_0^t - \sum_i i \int_0^t \left[n_i \langle \partial_t \phi_i | \phi_i \rangle + i \frac{dn_i}{dt} \right]. \quad (52)$$

It can be immediately seen that the terms $i [n_i]_0^t$ and $-i \int_0^t dn_i/dt$ cancel, and variation with respect to ϕ_i yields the usual KS equations for time-evolution of the orbitals, multiplied by n_i

$$n_i \left(-\frac{1}{2} \nabla^2 + V_{ext} + v_{ks} \right) \phi_i^* = i n_i \partial_t \phi_i^*, \quad (53)$$

which tells us nothing about the time-evolution of the occupation numbers.

Similarly, varying \mathcal{S} with respect to the occupation numbers yields

$$\langle \phi_i | -\frac{1}{2} \nabla^2 + V_{ext} + v_{ks} | \phi_i \rangle = -i \langle \phi_i | \partial_t \phi_i \rangle, \quad (54)$$

which is automatically satisfied by Eq. (53).

3.3 Solving for occupation numbers in the time independent case

In previous works, we showed that under a perturbation $V^{(1)}$, the occupation numbers change in time-independent degenerate perturbation theory to satisfy the equation [11, 19]

$$\langle \phi_k | V^{(1)} + v_{ks}^{(1)} | \phi_j \rangle = \frac{\delta_{jk}}{N_{\mathcal{D}_{m \in \mathcal{D}}}} \sum_{m \in \mathcal{D}} \langle \phi_m | V^{(1)} + v_{ks}^{(1)} | \phi_m \rangle, \quad (55)$$

where N_e is the total number of degenerate electrons, and $v_{ks}^{(1)}$ is the first-order Coulomb plus XC potential. For a time-dependent perturbation $v_{ks}^{(1)}$ is

$$v_{ks}^{(1)} = \int \frac{\delta v_{ks}(\mathbf{r}, t)}{\delta \rho(\mathbf{r}', t')} \rho^{(1)}(\mathbf{r}', t') d\mathbf{r}' dt' \equiv \frac{\partial v}{\partial \rho} \rho^{(1)}, \quad (56)$$

and we shall use the term on the far right as a shorthand for the middle expression. For a time-independent perturbation, the dependence on t and t' , as well as the integral over dt' can be omitted. In practice, most

functionals are local in time, and even for time-dependent perturbations, the form of $\mathbf{v}_{ks}^{(1)}$ is the same as in the time-independent case.

To solve for $n_i^{(1)}$, we can break up $\rho^{(1)}$ into two parts, like so

$$\rho^{(1)}(\mathbf{r}) = \sum_i \left[n_i 2\text{Re} \int \frac{\partial \phi_i(\mathbf{r})}{\partial V(\mathbf{r}')} V^{(1)}(\mathbf{r}') \phi_i(\mathbf{r}) d\mathbf{r}' + n_i^{(1)} \frac{\partial \rho(\mathbf{r})}{\partial n_i} \right] \equiv \rho_V^{(1)}(\mathbf{r}) + \sum_i n_i^{(1)} \frac{\partial \rho(\mathbf{r})}{\partial n_i}. \quad (57)$$

The derivative of ρ with respect to n_i is given by

$$\frac{\partial \rho(\mathbf{r})}{\partial n_i} = \phi_i(\mathbf{r})^* \phi_i(\mathbf{r}) + \sum_j n_j 2\text{Re} \frac{\partial \phi_j^*(\mathbf{r})}{\partial n_i} \phi_j(\mathbf{r}), \quad (58)$$

where the second term can be obtained from perturbation theory by considering a change in occupation numbers as the perturbation [25, 26].

Let us note that the second derivative of energy with respect to occupation numbers is

$$\frac{\partial^2 E}{\partial n_i \partial n_j} = \langle \phi_j | \frac{\partial \mathbf{v}}{\partial \rho} \frac{\partial \rho}{\partial n_i} | \phi_j \rangle \equiv H_{ij}, \quad (59)$$

where H_{ij} is a component of the matrix \mathbf{H} , the Hessian of the energy with respect to occupation numbers. To further simplify notation, we also define the vector

$$\mathbf{W}_k^{(1)} \equiv \sum_m \langle \phi_m | V^{(1)} + \frac{\partial \mathbf{v}}{\partial \rho} \rho_V^{(1)} | \phi_m \rangle \left(\frac{1}{N_{\mathcal{D}}} - \delta_{mk} \right). \quad (60)$$

We can then group the terms proportional to $n_i^{(1)}$ from Eq. (55) to get the matrix equation

$$\sum_i \left[H_{ki} - \frac{1}{N_D} \sum_{m \in \mathcal{D}} H_{mi} \right] n_i^{(1)} = W_k^{(1)}. \quad (61)$$

The matrix on the left-hand side is singular, which we can see from the Sherman-Morrison matrix inverse formula, by expressing the second term as $v_k u_i$, where $v_k = -1 \forall k$ and $u_i = 1/N_D \sum_m H_{mi}$, so that the full matrix can be written as $\mathbf{H} + \mathbf{v}^T \mathbf{u}$. The Sherman-Morrison formula has a denominator equal to $1 + \mathbf{v}^T \mathbf{H}^{-1} \mathbf{u}$, which in this case is zero. Therefore, this equation cannot be solved by matrix inversion.

However, we can note that, from its definition in Eq. (60), $\sum_k W_k^{(1)} = 0$. Additionally, because the number of electrons is conserved, we must also have $\sum_i n_i^{(1)} = 0$. This reduces the dimensionality of the vector space from $N_{\mathcal{D}}$ to $N_{\mathcal{D}} - 1$. We can generate an $N_{\mathcal{D}} \times N_{\mathcal{D}} - 1$ matrix of orthonormal column vectors that sum to zero, \mathbf{A} , and use it to project out the relevant subspace from our equation. Because $\sum_m H_{mi}$ is independent of

the index k , this term vanishes within that subspace, and we can solve for the first-order occupation numbers as

$$\mathbf{n}^{(1)} = \mathbf{A} [\mathbf{A}^T \mathbf{H} \mathbf{A}]^{-1} \mathbf{A}^T \mathbf{W}^{(1)}, \quad (62)$$

We can see that this equation behaves correctly where there is no degeneracy by noting that $\mathbf{n}^{(1)}$ necessarily vanishes when $N_{\mathcal{D}} = 1$, because $\mathbf{W}^{(1)}$ is identically zero. Therefore, the occupation numbers of non-degenerate orbitals remain fixed. In the next section, we will extend this time-independent expression by treating it as the lowest order term of a Taylor series in ω .

3.4 Solving for non adiabatic occupation numbers

As we have noted, degeneracy in a KS system does not imply degeneracy in the interacting system. degenerate eigenvalues do not split in KS DFT perturbation theory [11, 18, 19], and instead, the occupation numbers rearrange themselves to preserve degeneracy. If a small, time-independent perturbation, δV is

Assume that we have a Hamiltonian H_0 for which both the KS orbitals have a degenerate ground state. Now add a small perturbation δV . The degeneracy of the true Hamiltonian will be lifted, while the KS orbital eigenvalues remain degenerate. Note also that because the KS equations are nonlinear, the energy does not remain constant when electrons are moved between orbitals that are initially degenerate.

To develop a theory describing the non-adiabatic linear response of time evolution operators, we will write an expression for the linear response of the interacting density and compare it to the standard orbital linear response in KS DFT. We will then show that both expressions are natural extensions of the time-independent expressions at $\omega = 0$ through the same Taylor series in ω . We will then use this to extend the adiabatic occupation numbers in the same manner.

The electron density of an interacting system of N electrons, whose true ground-state wave function is $\Psi_0(\mathbf{r}_1 \dots \mathbf{r}_N)$ is given by the diagonal of its one-body density matrix, which we write

$$|\psi_0\rangle\langle\psi_0| = \int \Psi_0(\mathbf{r}, \mathbf{r}_2 \dots \mathbf{r}_N) \Psi_0^*(\mathbf{r}', \mathbf{r}_2 \dots \mathbf{r}_N) d\mathbf{r}_2 \dots d\mathbf{r}_N, \quad (63)$$

where we use the normalization $\langle\Psi_0|\Psi_0\rangle = N$.

We can put the one-body density matrix in the basis of KS orbitals, and if the KS system reproduces the exact electron density, we can write

$$\sum_{ij} [\langle\phi_i|\psi_0\rangle\langle\psi_0|\phi_j\rangle - n_i\delta_{ij}] \phi_i(\mathbf{r})\phi_j^*(\mathbf{r}) = 0, \quad (64)$$

or in other words, there is no difference between the electron density obtained from the exact one-body density matrix and from the KS system.

Under a perturbation, the KS system should continue to match the exact electron density. If we Eq. (64) to first-order in perturbation theory, several terms involving first-order KS orbitals cancel, and we are left

with the first-order interacting one-body density matrix in the basis of unperturbed KS orbitals minus the first-order KS density. Dropping the explicit \mathbf{r} dependence, we get

$$0 = 2\text{Re} \sum_{ij} \langle \phi_i | \psi_0^{(1)}(t) \rangle \langle \psi_0 | \phi_j \rangle \phi_i \phi_j^* - \rho_V^{(1)}(t) - \sum_i \int n_i^{(1)}(t') \left(\phi_i^* \phi_i \delta(t-t') + 2\text{Re} \frac{\partial \phi_i^*(t)}{\partial n_i(t')} \phi_i \right) dt', \quad (65)$$

where we have employed the definition from Section 3.3 for $\rho_V^{(1)}$, except now, we are considering time-dependent perturbations.

In most cases, this equation is satisfied with $n_i^{(1)} = 0$, and it is only for cases where we have degeneracy that we need first-order occupation numbers in the Kohn-Sham system. Therefore, when fractional occupation numbers aren't necessary, $\rho_V^{(1)}$ cancels every term in the interacting density.

If $\rho_V^{(1)}$ is equal to the interacting density, they must have poles at the same frequencies. To find the poles of the interacting density, we look at the linear response of the one-body density matrix in the basis of KS orbitals, which is

$$2\text{Re} \langle \phi_i | \psi_0^{(1)} \rangle \langle \psi_0 | \phi_j \rangle = \text{Re} \sum_n \langle \Psi_a | V^{(1)}(\omega) | \Psi_0 \rangle \langle \phi_i | \psi_n \rangle \langle \psi_0 | \phi_j \rangle \left(\frac{1}{E_0 - E_n + \omega} + \frac{1}{E_0 - E_n - \omega} \right), \quad (66)$$

and this equation has poles at $\omega = \pm(E_0 - E_n)$. Therefore, $\rho_V^{(1)}$ has poles at every $\pm(E_0 - E_n)$.

The poles of $\rho_V^{(1)}$ can be obtained from the linear response of the KS orbitals as the singularities of the matrix [7]

$$\sum_{jb} \left[\delta_{ij} \delta_{ab} + \langle \phi_a | \frac{\delta v_{ks}}{\delta \rho} \phi_j \phi_b | \phi_i \rangle \left(\frac{1}{\epsilon_i - \epsilon_a + \omega} + \frac{1}{\epsilon_i - \epsilon_a - \omega} \right) \right] \rho_{Vjb}^{(1)} = \langle \phi_a | V^{(1)}(\omega) | \phi_i \rangle \left(\frac{1}{\epsilon_i - \epsilon_a + \omega} + \frac{1}{\epsilon_i - \epsilon_a - \omega} \right), \quad (67)$$

which after some algebraic manipulation becomes

$$\left[\delta_{ij} \delta_{ab} \left((\epsilon_i - \epsilon_a) - \frac{\omega^2}{2(\epsilon_i - \epsilon_a)} \right) + \langle \phi_a | \frac{\delta v_{ks}}{\delta \rho} \phi_j \phi_b | \phi_i \rangle \right]^{-1} \langle \phi_a | V^{(1)}(\omega) | \phi_i \rangle = \rho_{Vjb}^{(1)}, \quad (68)$$

where the inverse is a matrix inverse of where the matrix has composite indices ia and jb . This matrix is independent of the perturbing potential, and therefore, so are the frequencies at which it becomes singular.

However, if there are certain states that aren't accessible as excitations of the initial occupation numbers, then there are certain poles at $E_0 - E_n$ for some set of $n \in D$, where the interacting density has poles but

$2\text{Re}\phi_i^{*(1)}\phi_i$ does not. Therefore terms must be canceled by poles in the term involving first-order occupation numbers. The terms in the first-order density proportional to $n_i^{(1)}$ are

$$\sum_i n_i^{(1)} \left(\phi_i^* \phi_i + 2\text{Re} \sum_{ak} \phi_a^* \phi_k \left[\delta_{kj} \delta_{ab} \left((\varepsilon_k - \varepsilon_a) - \frac{\omega^2}{2(\varepsilon_k - \varepsilon_a)} \right) + \langle \phi_a | \frac{\delta v_{ks}}{\delta \rho} \phi_j \phi_b | \phi_k \rangle \right]^{-1} \langle \phi_a | \frac{\delta v_{ks}}{\delta \rho} \phi_i \phi_i | \phi_k \rangle \right), \quad (69)$$

where the second term comes from explicitly expanding $\langle \phi_k^{(1)} | \phi_j \rangle$ in perturbation theory as in Eq. (68). This expression clearly has poles in the second term at the same location as $\rho_{Vjb}^{(1)}$. Therefore, any additional poles must be present in $n_i^{(1)}$ itself.

Although explicitly finding the terms that $n_i^{(1)}$ must cancel requires knowing the true wave function, we know from time-independent perturbation theory what the result should be in the adiabatic limit. In the limit that $\omega \rightarrow 0$, the occupation numbers are determined by the solution to Eq. (62).

We can better compare our expression for the adiabatic limit of $n_i^{(1)}$ to the behavior of the true wave function in the adiabatic limit by making the Taylor series expansion

$$\frac{1}{E_0 - E_n + \omega} + \frac{1}{E_0 - E_n - \omega} = \sum_{m=0}^{\infty} \frac{2\omega^{2m}}{(E_0 - E_n)^{2m+1}} \quad (70)$$

Equation (62) includes only the $m = 0$ term from this series. It should be noted that the denominator $E_0 - E_n$ is the second order change in energy if a rotation is applied between Ψ_0 and Ψ_n . Likewise, The Hessian can be used to calculate the second-order energy for moving electrons between degenerate orbitals by changing their occupation numbers, given by $1/2\delta\mathbf{n}^T \mathbf{H} \delta\mathbf{n}$. Because δn sums to zero when the number of electrons is conserved, this suggests that $\mathbf{A}^T \mathbf{H} \mathbf{A}$, which appears in Eq. (62), is the analog of $2(E_n - E_0)$. Making this substitution into the Taylor series, we get

$$\mathbf{M}(\omega) \equiv \sum_{m=0}^{\infty} 2^{2m+2} \omega^{2m} [\mathbf{A}^T \mathbf{H} \mathbf{A}]^{-2m-1} = \left[\frac{1}{2} \mathbf{A}^T \mathbf{H} \mathbf{A} + \omega \mathbf{I} \right]^{-1} + \left[\frac{1}{2} \mathbf{A}^T \mathbf{H} \mathbf{A} - \omega \mathbf{I} \right]^{-1}, \quad (71)$$

where \mathbf{I} is the identity matrix. We can match the time-independent expression when $\omega = 0$ by writing the linear response of the occupation numbers as

$$\mathbf{n}^{(1)}(\omega) = \frac{1}{4} \mathbf{A} \mathbf{M}(\omega) \mathbf{A}^T \mathbf{W}^{(1)}(\omega). \quad (72)$$

Equation (72) is coupled to the standard TDDFT equations through the term $\rho_\phi^{(1)}(\omega)$, and both must be solved simultaneously to find the time-dependent occupation numbers. However the poles of Eq. (72), which arise at the singular points of \mathbf{M} , are determined by the eigenvalues of $1/2\mathbf{A}^T \mathbf{H} \mathbf{A}$, which depends only on unperturbed orbitals from within the degenerate space. Similarly, the standard linear response equations do not depend on Eq. (72), and therefore, the poles obtained from the two sets of equations are independent of one another.

3.5 Excitations in atomic iron

In Table 1, we have applied this method to atomic iron as calculated with Slater exchange and VWN correlation, using the Def2-TZVP basis set and complex spherical harmonics. From our initial ground state self-consistent field (SCF) calculation in spherical symmetry, we found that the $3d$ beta orbitals contain 0.279 electrons each and are degenerate with the $4s$ beta orbital, which contains 0.607 electrons.

The perturbation calculations required for computing the Hessian involve a coupled-perturbed term that mixes nondegenerate orbitals with different occupation numbers. In our previous work on degenerate perturbation theory [11, 19], we have neglected these terms because of the additional computational complexity they introduce. However, our newly developed code is capable of solving the coupled-perturbed equations, and so they are included in this work.

To test the effects these previously neglected terms, we carried out two different calculations: one with an “unrelaxed” Hessian, where we did not include the coupled-perturbed terms that mix nondegenerate orbitals, and one with a “relaxed” Hessian, where this term was included. Both Hessians generated the same eigenvectors, but the first eigenvalue, corresponding to movement of electrons between the $3d$ and $4s$ orbitals, was smaller by a factor of 3.68 in the relaxed Hessian. The remaining two non-zero eigenvalues differed by less than twenty percent between the two Hessians.

We also tested these Hessians by making comparisons to numerical energy differences found with Dr. Dunlap’s code. Because Dr. Dunlap’s code cannot break spherical symmetry, the only numerical test we could perform was for d to s transitions, where electrons are taken equally from every d orbital.

We tested energy differences for both the relaxed and unrelaxed Hessians, while adding between zero and 0.2 electrons to the $3d$ orbital. In the former test, occupation numbers were changed and new energies were computed with the same set of orbitals, while in the later, they were allowed to relax under a new SCF calculation. For the unrelaxed calculation, the exact energy differences matched those from perturbation theory almost exactly over the range we tested. For the relaxed calculation, the energies from perturbation theory were slightly larger than those from the SCF calculation, although there was still good agreement between the two sets of numbers. The results of this test are plotted in Figure 3.

The eigenvalues of $1/2\mathbf{A}^T\mathbf{H}\mathbf{A}$ are given in the first row in cm^{-1} , and the eigenvectors, transformed back into the full 6 dimensional basis of degenerate orbitals, are given in the columns below, with the label of the associated orbital in the column on the far left.

The first eigenvector, with an eigenvalue of 7017.3 cm^{-1} , corresponds to a $4s$ - $3d$ transition and is not an eigenvector of \mathbf{H} . It is, however, a right-eigenvector of $\left[H_{ki} - \frac{1}{N_D} \sum_{m \in \mathcal{D}} H_{mi}\right]$. The Hessian, on the other hand, has no eigenvectors that both sum to zero and involve $d - s$ transitions and no eigenvectors with this eigenvalue.

The remaining eigenvectors correspond to transitions between d orbitals. The last two eigenvectors are degenerate, with an eigenvalue of zero. Their degeneracy allows us to form them into equivalent linear combinations, and we have chosen a basis that highlights the reason that the eigenvalues are zero. In this basis, one eigenvector corresponds to the movements of electrons $d^{-2} \leftrightarrow d^2$ and the other corresponds to movements of $d^{-1} \leftrightarrow d^1$. Because the magnitude squared of d^{+m} and d^{-m} are equal at every point in space,

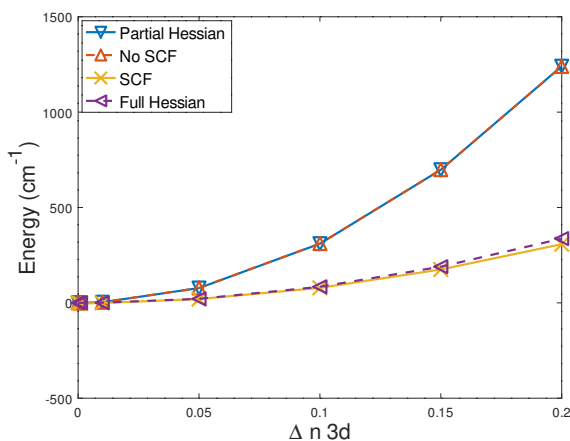


Fig. 3 — Change in energy as electrons are moved from the $4s$ orbital into the $3d$ orbitals.

Table 1 — Poles and eigenvectors for occupation number transitions in atomic iron

ω (cm^{-1})	7017.3	4213.7	2091.5	0.0	0.0
$3d^{-2}$	0.1826	0.5345	0.1195	-0.7071	0.0000
$3d^{-1}$	0.1826	-0.2673	-0.4781	0.0000	-0.7071
$3d^0$	0.1826	-0.5345	0.7171	0.0000	0.0000
$3d^1$	0.1826	-0.2673	-0.4781	0.0000	0.7071
$3d^2$	0.1826	0.5345	0.1195	0.7071	0.0000
$4s$	-0.9129	0.0000	0.0000	0.0000	0.0000

moving along either of the degenerate eigenvectors leaves the electron density, and therefore the energy, unchanged.

A direct comparison of excitation energies to experiment is difficult, because excitation energies depend both on orbital angular momentum, L and total angular momentum, J . The DFT description is based on a single-particle picture, and therefore does not have the form necessary to generate angular momentum eigenstates. In the general case of more than one electron is in a set of fractionally occupied orbitals, there is not even a unique mapping between the electron density of the Kohn-Sham system and an average over Slater determinants. It is impossible, then, to say whether a transition between two different d orbitals should correspond to a particular line in the spectrum of iron.

We have attempted to make some comparison in Table 2, where the poles we obtained using the relaxed and unrelaxed Hessians are compared to the most reasonably analogous experimental excitation energies [27]. The lowest experimental excitation energy from the $3d^6 4s^2$ state to the $3d^7 4s$ state with the same spin multiplicity as the ground state (multiplicity 5) is at 6928.3 cm^{-1} , although depending J , can be as high as 8154.7 cm^{-1} . This is in rough agreement with the $4s$ - $3d$ transition energy we computed.

Table 2 — Comparison of poles and excitation energies from calculations based on a relaxed Hessian, an unrelaxed Hessian, and the experimental line spectrum

ω (relaxed) (cm^{-1})	7017.3	4213.7	2091.5	0.0	0.0
ω (unrelaxed) (cm^{-1})	25846.9	4960.3	-2050.7	0.0	0.0
Experimental (cm^{-1})	6928.3		415.9-978.0		

For eigenvectors corresponding to transitions between different $3d$ orbitals, the most reasonable experimental candidates for comparison spectrum would seem to be the different J states of the $3d^6 4s^2$ configuration. The ground state of iron has $J = 4$, but $J = 3, 2$, or 1 states are also possible. The excitation energies to these states range between 415.9 and 978.1 cm^{-1} , which is significantly smaller than the numbers from our calculation. However, given that the single-particle picture of DFT is not good at modeling complicated open-shell states, and DFT is known to frequently fail at describing transition metals, perhaps we should not expect good agreement here.

3.6 Summary of time-dependent occupation number DFT

Occupation numbers only change in perturbation theory when the unperturbed state is degenerate. This is because the terms in perturbation theory come from a Taylor series in the strength of the perturbing potential. With the exception of a small region in which degeneracy can be achieved by adjusting occupation numbers, the occupation numbers tend to have constant values of either one or zero. When the occupation numbers are constant, all of their derivatives to any order with respect to the coupling strength are zero. Therefore, it is impossible to build a Taylor series that starts from a non-degenerate point, where occupation numbers are constant that passes through a degenerate point, where they must shift. Likewise, a Taylor series starting at a degenerate point will only be valid until the occupation numbers become one or zero.

Time-dependent occupation numbers are a necessity in KS DFT to connect time-dependent and time-independent perturbation theory via the adiabatic theorem. Because the denominator matrices in the equations for the first-order occupation numbers do not couple to those of standard linear response TDDFT, they each provide an independent set of poles corresponding to different excitation energies. Preliminary work on atomic iron indicates that the poles of the first-order occupation numbers predict meaningful transition energies.

4. DFT CODE DETAILS

A perturbation theory code for DFT, written in C, was developed to interface with Dr. Brett Dunlap’s SCF code. Dr. Dunlap’s code performs an SCF calculation on an atom in spherical symmetry, and the perturbation code loads the result, then computes the response to a potentially symmetry-breaking perturbation.

In this chapter, we will discuss the numerical implementation of the various integrals and transformations utilized by the perturbation theory code. The code first loads a basis set, molecular orbital transformation matrix, and set of eigenvalues from the output of Dr. Dunlap’s program. It then performs perturbation calculations on the molecular orbitals, which are expanded from a purely spherical basis into a basis of spherically symmetric functions times spherical harmonics.

Because the initial SCF calculation is performed in spherical symmetry, there are various numerical simplifications that can be utilized, even though the perturbation calculation requires symmetry-breaking integrals. The angular portion of the exchange-correlation integrals can be performed analytically, unlike in most codes, because even the symmetry breaking portions are a product of spherical harmonics. Numerical integration only has to be performed over the radial coordinate. The Coulomb integral is somewhat easier to perform as well, because all orbitals in the integral are located at the same atomic center. Below, the numerical techniques are detailed for performing the Coulomb and exchange-correlation integrals and for transforming them into the molecular orbital basis.

4.1 Basis functions, atomic orbitals, and molecular orbitals

Electronic structure calculations are typically carried out in a basis of Gaussian-type atomic orbitals. The radial portion of a Gaussian-type atomic basis function is a sum over atom-centered Gaussians multiplied by r^l . The angular portion of the basis function is the spherical harmonic $Y_l^m(\theta, \phi)$. The entire basis function, $\chi_m(\mathbf{r})$ can then be written as

$$\chi_\mu(\mathbf{r}) = Y_l^m(\theta, \phi) \sum_j A_{j\mu} r^j e^{-\zeta_j r^2}, \quad (73)$$

where l is the angular momentum of the orbital.

The molecular orbitals are taken to be a linear combination of basis functions and are given by

$$\phi_i(\mathbf{r}) = \sum_\mu C_{\mu i} \chi_\mu(\mathbf{r}), \quad (74)$$

and the Kohn-Sham equations in this basis become

$$\sum_\nu C_{\nu i} \langle \chi_\mu | -\frac{1}{2} \nabla^2 + V(\mathbf{r}) + v_{ks}(\mathbf{r}) | \chi_\nu \rangle = \varepsilon_i \sum_\nu C_{\nu i} \langle \chi_\mu | \chi_\nu \rangle. \quad (75)$$

If the basis is orthonormal, the overlap matrix $\langle \chi_\mu | \chi_\nu \rangle$ becomes $\delta_{\mu\nu}$. The first-order equations for $C_{\nu i}^{(1)}$ in time-independent perturbation theory are

$$\frac{\sum_\nu C_{\mu a}^* C_{\nu i} \langle \chi_\mu | V^{(1)}(\mathbf{r}) + \sum_{\alpha\beta k} \left(2\text{Re} n_i C_{\alpha k}^{*(1)} C_{\beta k} + n_i^{(1)} C_{\alpha k}^* C_{\beta k} \right) \int \frac{\delta v_{ks}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \chi_\alpha(\mathbf{r}') \chi_\beta(\mathbf{r}') d\mathbf{r}' | \chi_\nu \rangle}{\varepsilon_i - \varepsilon_a} = \sum_{\mu\nu} C_{\nu i}^{(1)} C_{\mu a}^* \langle \chi_\mu | \chi_\nu \rangle, \quad (76)$$

And it can be seen, therefore, that integrals involving four atomic basis functions must be evaluated to compute the Coulomb and exchange-correlation terms.

4.2 Electron-electron interaction integrals between atomic basis functions

The evaluation of Coulomb integrals and exchange-correlation integrals both require integrating products of four orbitals and an additional term over all space. Below, we describe the computational details of how these are carried out in our code.

The Coulomb integral involves products of four orbitals with the kernel $1/|\mathbf{r} - \mathbf{r}'|$. If \mathbf{r} and \mathbf{r}' are vectors centered at the same origin, the Coulomb kernel can equivalently be written as

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{1}{\sqrt{(\mathbf{r} - \mathbf{r}') \cdot (\mathbf{r} - \mathbf{r}')}} = \frac{1}{\sqrt{r^2 + r'^2 - 2rr' \cos \gamma}}, \quad (77)$$

where r and r' are the magnitude of vectors \mathbf{r} and \mathbf{r}' , and γ is the angle between them. This expression can be expanded in terms of Legendre polynomials to get

$$\frac{1}{\sqrt{r^2 + r'^2 - 2rr' \cos \gamma}} = \sum_{l=0}^{\infty} \frac{r_{<}^l}{r_{>}^{l+1}} P_l(\cos \gamma), \quad (78)$$

where $r_{>}$ is the greater of r and r' , and $r_{<}$ is the lesser of r and r' .

Because the angular portion of an atomic orbital is a spherical harmonic, and the spherical harmonics form an orthonormal basis, it is useful to project the above expression onto a basis of spherical harmonics. Doing so yields

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_l^{*m}(\theta', \phi') Y_l^m(\theta, \phi), \quad (79)$$

where θ , ϕ , and θ' , ϕ' are the angular portions of the spherical coordinates of \mathbf{r} and \mathbf{r}' .

The radial and angular portions of the Coulomb integral between four atomic basis functions separate. Keeping in mind that the Jacobian for spherical coordinates is $r^2 \sin \phi$, the Coulomb integral can then be written as

$$\begin{aligned} \int \frac{\chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' &= 4\pi \sum_{jkpq} A_{j\mu} A_{k\nu} A_{p\alpha} A_{q\beta} \sum_{l=0}^{\infty} \int \frac{e^{-(\zeta_j + \zeta_k)r^2 - (\zeta_p + \zeta_q)r'^2}}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} r^{l_1+l_2+2} r'^{l_3+l_4+2} dr dr' \\ &\times \sum_{m=-l}^l \int Y_{l_1}^{*m_1}(\theta', \phi') Y_{l_2}^{*m_2}(\theta', \phi') Y_l^m(\theta', \phi') \sin \phi' d\theta' d\phi' \int Y_l^m(\theta, \phi) Y_{l_3}^{m_3}(\theta, \phi) Y_{l_4}^{m_4}(\theta, \phi) \sin \phi d\theta d\phi. \end{aligned} \quad (80)$$

A single radial integration can be performed analytically over either r or r' . Because $r_{>}$ and $r_{<}$ can both be either r or r' , the integral must be split into two parts: one when $r < r'$ and one where $r > r'$. If the analytic integral is performed over r' , this becomes

$$\int_0^r \frac{e^{-(\zeta_j + \zeta_k)r^2 - (\zeta_p + \zeta_q)r'^2}}{2l+1} r^{l_1+l_2-l+1} r'^{l_3+l_4+2} dr' + \int_r^{\infty} \frac{e^{-(\zeta_j + \zeta_k)r^2 - (\zeta_p + \zeta_q)r'^2}}{2l+1} r^{l_1+l_2+l+2} r'^{l_3+l_4-l+1} dr'. \quad (81)$$

The solution to this integral is in terms of the incomplete Gamma function

$$\Gamma(a, x) = \int_x^\infty e^{-t} t^{a-1} dt. \quad (82)$$

as

$$\begin{aligned} \frac{1}{2} e^{-(\zeta_j + \zeta_k)r^2} \left[(\zeta_p + \zeta_q)^{-\frac{l+l_3+l_4+3}{2}} \left(\Gamma((\zeta_p + \zeta_q)r^2) - \Gamma\left(\frac{l+l_3+l_4+3}{2}, (\zeta_j + \zeta_k)r^2\right) \right) r^{l_1+l_2-l+1} \right. \\ \left. + (\zeta_p + \zeta_q)^{-\frac{l-l_3-l_4-2}{2}} \Gamma\left(\frac{-l+l_3+l_4+2}{2}, (\zeta_p + \zeta_q)r^2\right) r^{l_1+l_2+l+2} \right], \end{aligned} \quad (83)$$

where $\Gamma((\zeta_p + \zeta_q)r^2)$ is the regular Gamma function.

The angular integrals over θ , θ' , ϕ , and ϕ' can be recast in terms of Wigner 3-j symbols, using the identity

$$\int Y_{l_1}^{m_1}(\phi, \theta) Y_{l_2}^{m_2}(\phi, \theta) Y_l^m(\phi, \theta) \sin \phi d\theta d\phi = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix}. \quad (84)$$

The Wigner-3j symbols are only nonzero if

$$\begin{aligned} |l_1 - l_2| \leq l \leq l_1 + l_2 \\ m_1 + m_2 = m, \end{aligned} \quad (85)$$

which restricts the number of integrals that need to be computed. For the integral in Eq. 84 to be non-zero, this condition must also be obeyed by l_3, l_4 and m_3, m_4 for the same l, m .

Once the radial and angular integrals are computed and stored, the radial integral for a given l must be paired with the corresponding sum of angular integrals from $m = -l$ to l . The product of these two terms can then be summed over all l to find the Coulomb integral between atomic basis functions.

The exchange correlation integrals are simpler, because first, for a local or semi-local density functional, they only depend on one coordinate, \mathbf{r} , rather than \mathbf{r} and \mathbf{r}' , and second, our initial SCF solution is spherically symmetric. For a local density functional, like VWN, the exchange correlation kernel is

$$\frac{\delta^2 E_{xc}}{\delta^2 \rho(\mathbf{r})} \equiv \frac{\partial V_{xc}(\mathbf{r})}{\partial \rho(\mathbf{r})}, \quad (86)$$

and the integrals needed for perturbation theory have the form

$$\langle \phi_i | \frac{\delta V_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r})} \phi_j^*(\mathbf{r}) \phi_j(\mathbf{r}) | \phi_i \rangle = \int \frac{\partial V_{xc}(\mathbf{r})}{\partial \rho(\mathbf{r})} \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r}) \phi_j^*(\mathbf{r}) \phi_j(\mathbf{r}) d\mathbf{r}, \quad (87)$$

which can be constructed from integrals of atomic basis functions of the form

$$\int \frac{\delta V_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r})} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) \chi_\alpha(\mathbf{r}) \chi_\beta(\mathbf{r}) d\mathbf{r}. \quad (88)$$

The exchange correlation kernel is spherically symmetric, so the only angular factors come from the four basis functions. Putting the basis functions into an explicit form and separating the radial and angular portions of the integral, we get

$$\sum_{jkpq} A_{j\mu} A_{kv} A_{p\alpha} A_{q\beta} \int \frac{\delta V_{xc}(r)}{\delta \rho(r)} r^{l_1+l_2+l_3+l_4} e^{-(\zeta_\mu+\zeta_\nu+\zeta_\alpha+\zeta_\beta)r^2} dr \int Y_{l_1}^{m_1}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) Y_{l_3}^{m_3}(\theta, \phi) Y_{l_4}^{m_4}(\theta, \phi) d\theta d\phi. \quad (89)$$

To perform the angular integral, it is easiest to use the Wigner 3-j coefficients to project the pairs $Y_{l_1}^{m_1} Y_{l_2}^{m_2}$ and $Y_{l_3}^{m_3} Y_{l_4}^{m_4}$ onto a basis of single spherical harmonics using Eq. (84). We then have

$$\begin{aligned} Y_{l_1}^{m_1}(\phi, \theta) Y_{l_2}^{m_2}(\phi, \theta) &= \sum_{l=|l_1-l_2|}^{l_1+l_2} \sum_{m=-l}^l K_{1lm} Y_l^m(\theta, \phi) \\ Y_{l_3}^{m_3}(\phi, \theta) Y_{l_4}^{m_4}(\phi, \theta) &= \sum_{l=|l_3-l_4|}^{l_3+l_4} \sum_{m=-l}^l K_{2lm} Y_l^m(\theta, \phi), \end{aligned} \quad (90)$$

where K_{1lm} and K_{2lm} are the projection coefficients. By the orthonormality of spherical harmonics, we then have

$$\begin{aligned} \int Y_{l_1}^{m_1}(\theta, \phi) Y_{l_2}^{m_2}(\theta, \phi) Y_{l_3}^{m_3}(\theta, \phi) Y_{l_4}^{m_4}(\theta, \phi) d\theta d\phi &= \frac{\sqrt{(2l_1+1)(2l_2+1)(2l_3+1)(2l_4+1)}}{4\pi} \\ &\times \sum_{lm} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} l_3 & l_4 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_3 & l_4 & l \\ m_3 & m_4 & m \end{pmatrix} \end{aligned} \quad (91)$$

The remaining radial portion of the integral can be computed numerically.

4.3 Numerical integration

For both the Coulomb and XC integrals, numerical integration over a single radial coordinate is required. Generally speaking, the integral from $r = 0$ to ∞ can be transformed into the range 0 to 1 by a coordinate transformation $r \rightarrow r(x)$, where $0 \leq x \leq 1$. Approximating the integral by numeric quadrature, we have

$$\int_0^\infty f(r) dr = \int_0^1 f(r(x)) \frac{dr}{dx} dx \approx \sum_i w_i f(r(x_i)) \frac{dr(x_i)}{dx_i}, \quad (92)$$

where w_i is a weight associated with the point x_i in the numerical integration scheme.

We use the parameter-free n -point radial integration grid of Köster et al. [28]. For a grid with n points along the radial axis, this scheme defines

$$x_i = \frac{n+1-2i}{n+1} + \frac{2}{\pi} \left[1 + \frac{2}{3} \sin^2 \left(\frac{i\pi}{n+1} \right) \right] \cos \left(\frac{i\pi}{n+1} \right) \sin \left(\frac{i\pi}{n+1} \right) \quad (93)$$

so that for $i = 0$, $x = 1$, and for $i = n$, $x = 0$. The function $r(x_i)$ is given by

$$r = \frac{1}{\ln 2} \ln \left(\frac{2}{1-x_i} \right), \quad (94)$$

which has the Jacobian

$$\frac{dr}{dx} = \frac{1}{\ln 2} \frac{1}{1-x_i}. \quad (95)$$

The weights in this scheme are

$$w_i = \frac{16}{3(n+1)} \sin^4 \left(\frac{i\pi}{n+1} \right), \quad (96)$$

and the integral is then approximated numerically as

$$\int_0^\infty f(r) dr \approx \sum_{i=1}^n \frac{16}{3(n+1) \ln 2} \sin^4 \left(\frac{i\pi}{n+1} \right) \frac{f(r(x_i))}{1-x_i} \quad (97)$$

4.4 Transforming to the molecular orbital basis

A tensor M_{ijkl} that linear function of molecular orbitals ϕ_i , ϕ_j , ϕ_k , and ϕ_l can be written in terms of atomic basis functions as

$$M_{ijkl} = \sum_{\mu\nu\alpha\beta} C_{\mu i} C_{\nu j} C_{\alpha k} C_{\beta l} M_{\mu\nu\alpha\beta}, \quad (98)$$

where $M_{\mu\nu\alpha\beta}$ is in the matrix in the atomic basis.

For example, the Coulomb integral between molecular orbitals $\phi_i(\mathbf{r})$, $\phi_j(\mathbf{r})$, $\phi_k(\mathbf{r}')$, and $\phi_l(\mathbf{r}')$ can be written as

$$\int \frac{\phi_i(\mathbf{r}) \phi_j(\mathbf{r}) \phi_k(\mathbf{r}') \phi_l(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' = \sum_{\mu\nu\alpha\beta} C_{\mu i} C_{\nu j} C_{\alpha k} C_{\beta l} \int \frac{\chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}) \chi_\alpha(\mathbf{r}') \chi_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (99)$$

The perturbation theory code performs the appropriate Coulomb and exchange-correlation integrals in the basis of atomic orbitals and then transforms them as above into the basis of molecular orbitals. If the entire transformation were performed at once, it would require eight nested loops, over i , j , k , l , μ , ν , α ,

and β . The computational time to make this transformation would then be $\mathcal{O}(N^8)$, where N is the number of basis functions.

If we refer to Eq. (98), however, it is apparent that $C_{\mu i}$ is a Jacobian matrix that defines a transformation between two coordinate bases. Such transformations can be performed on a single index of M at a time, and doing the transformation in this manner reduces the computational time to $\mathcal{O}(N^5)$. For example, if we apply the transformation only to the last index, we have

$$M_{\mu\nu\alpha l} = \sum_{\beta} C_{\beta l} M_{\mu\nu\alpha\beta}, \quad (100)$$

which requires only five nested loops to sum over l , μ , ν , α , and β . This can then be repeated three more times for the remaining pairs of indices.

Because the original SCF calculation is performed in spherical symmetry, the matrix $C_{\mu i}$ is stored in block-diagonal form, with consecutive blocks for s , p , d , f , etc. orbitals. Each block contains occupied orbitals, followed by virtual orbitals. The matrix only describes the radial portion of the transformation and does not differentiate between orbitals with different m -values of the spherical harmonics. Therefore, when the Coulomb and exchange-correlation integrals are performed, an additional nested loop is required for each spherically symmetric orbital to multiply it by all $2l + 1$ possible $Y_l^m(\theta, \phi)$.

For the exchange correlation integrals, the radial portion of the integrals depend only on the angular momentum of each individual orbital and not on the total angular momentum of the product of orbitals. Therefore, only a single radial integral is required for each product of four atomic basis functions. The radial portion of the Coulomb integrals, on the other hand, depend on Wigner-3j symbols, which are a function of the total angular momentum l . Therefore, one Coulomb integral must be performed for each possible l , such that $|l_1 - l_2| \leq l \leq l_1 + l_2$ and $|l_3 - l_4| \leq l \leq l_3 + l_4$ and they must be multiplied by the appropriate angular factors and summed during the transformation to molecular orbitals.

5. CONCLUSIONS

We have developed two electrochemically-relevant perturbation theories, one for electrochemical mean-field theory and one for DFT. The first takes inspiration from DFT and treats the chemical potential in a manner similar to DFT's Coulomb and exchange-correlation potentials. We split the chemical potential one component that is known exactly, the chemical potential of an ideal solution, and one component which must be approximated by some sort of interaction term. The first-derivatives obtained from the perturbation theory that we have developed allow for the use of numerical integration techniques to find an essentially exact solution to the mean-field equations.

The second DFT perturbation theory we developed extends our previous work on degenerate perturbation theory to the time-dependent case. Because Marcus theory indicates that electron transfer happens between degenerate states, this perturbation theory can provide insight into the dynamics of electron-transfer processes. We have shown that typical time-dependent DFT misses certain excitations that are present in degenerate systems and have that our theory approximately predicts the $3d-4s$ transition energy for atomic iron.

In the course of this project, two computational codes were developed. The first, an electrochemical mean-field theory code, was developed in Matlab. It solves for the concentration of the components of a solution composed of two ionic species between capacitor plates with planar symmetry. It could be potentially extended to two and three dimensional systems by the use of Gaussian or plane-wave basis sets. It would also be possible to improve the approximations used for the interaction portion of the chemical potential by adding additional terms, for example to account for a finite ion radius.

The second code interfaces with an existing SCF code developed by Dr. Brett Dunlap. It loads the results of the SCF calculation for spherical atoms, computes Coulomb and exchange-correlation integrals, and solves the coupled-perturbed KS equations necessary for DFT perturbation theory.

The electrochemical mean-field and DFT perturbation theories both have the same form because they are both first-order approximations to a nonlinear set of equations. Because of their similarity and because of the freedom to choose different approximations to the interacting chemical potential, it is hoped that this work will lead to a closer connection between the two theories, where DFT parameters are used to inform larger scale electrochemical calculations.

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