An Algorithmically Determined Exchange-Correlation (ADEXC) Method for Electronic Structure Calculations

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***Abstract*—We present a novel approach to Inverse Density Functional Theory (IDFT) based on constrained-optimization and the adjoint state method, the Algorithmically Determined Exchange Correlation (ADEXC) technique. A density mismatch functional is minimized subject to constraints on the only other Kohn-Sham observables with physical meaning, the ionization potential and total energy. We employ an Augmented-Lagrangian approach to circumvent computing dense Hessians.**

I. Introduction

Density Functional Theory (DFT) is one of the most widely adopted frameworks for modeling many-body quantum systems from first principles. Traditionally, DFT operates in a forward manner: starting from an electron configuration, it computes the ground-state density and corresponding potential, including the crucial exchange-correlation component [1]. This approach has become central to modern materials modeling and aligns well with the concept of a "digital twin", where properties of materials can be simulated and analyzed *in silico*, often before any physical synthesis.

However, leveraging this paradigm for design and discovery—where one begins with a target property or density and seeks the configurations that yield it—requires solving the inverse problem. Inverse Density Functional Theory (IDFT) addresses this challenge by reconstructing the exchange-correlation potential from a given electron density [2]. Despite its theoretical appeal, current implementations of IDFT struggle to consistently recover known exchange-correlation functionals, even in well-understood systems.

This shortcoming presents both theoretical and practical obstacles. Theoretically, the Hohenberg-Kohn theorems [3] guarantee that each ground-state density corresponds to a unique external potential (up to a constant), implying that a well-posed IDFT should exist. Practically, however, the inverse problem is notoriously ill-conditioned: small variations in the input density can lead to large fluctuations in the reconstructed potential. This sensitivity poses a major challenge for any empirical or data-driven effort to model the exchange-correlation functional. Without a stable and reliable inversion procedure, it becomes difficult to validate known functionals, extract meaningful trends from data, or develop accurate analytic approximations. As a result, the full potential of IDFT remains largely untapped for engineering applications and materials design.

Our solution is to constrain the inversion procedure to the observables of the Kohn-Sham system which have physical correspondences; the ground-state total energy and the ionization potential related to the HOMO level. To this end, we employ a constrained optimization approach, where variational derivatives of a density mismatch objective in conjunction with energy constraints are computed via adjoint-state equations. In order to circumvent the computation of dense hessians we utilized the augmented-Lagrangian technique to incorporate constraints into a first-order optimization.

II. Adjoints for the Dominant General Eigendecomposition

To compute exact gradients within our DFT simulation code NESSIE [4], [5], any differentiation scheme must account for the fact that NESSIE operates on a finite-element discretization and evaluates the solution over a selected subset of relevant eigenmodes. Thus we derive the adjoints of the dominant general eigendecomposition in a similar manner to the standard formulation in Ref. 6.

The variation of the loss, L, on some electron density ρ with, respect to an internal potential V is given by:

$$\frac{\delta L[\rho(V(x))]}{\delta V(x)}. \tag{1}$$

Let $\mathbf{V} = (V_1, V_2, ..., V_n)$ denote the discretized potential, and let $\mathbf{P}$ and $\mathbf{L}$ represent the discretized electron density and loss function, respectively. The variation of the loss with respect to $\mathbf{V}$ yields the following gradient:

$$\nabla \mathbf{L}[\mathbf{P}(\mathbf{V})] = (\frac{\partial \mathbf{L}[\mathbf{P}(\mathbf{V})]}{\partial V_1}, \frac{\partial \mathbf{L}[\mathbf{P}(\mathbf{V})]}{\partial V_2}, ..., \frac{\partial \mathbf{L}[\mathbf{P}(\mathbf{V})]}{\partial V_n}). \tag{2}$$

In reverse mode notation $\nabla \mathbf{L}[\mathbf{P}(\mathbf{V})]$ is $\overline{\mathbf{V}}$. Stated otherwise, the variation of the loss on the density with respect to the internal potential is the *adjoint of the internal potential*.

Via the adjoint state method [6], [7], we obtain:

$$\overline{\mathbf{V}} = \overline{E}\boldsymbol{\Psi}^\top \frac{\partial \mathbf{H}}{\partial V}\boldsymbol{\Psi} - \boldsymbol{\Xi}^\top \frac{\partial \mathbf{H}}{\partial V}\boldsymbol{\Psi}, \tag{3}$$

where:

$$(\mathbf{H} - E\mathbf{S})\boldsymbol{\Xi} = (I - \mathbf{S}\boldsymbol{\Psi}\boldsymbol{\Psi}^\top)\overline{\boldsymbol{\Psi}}, \tag{4}$$

and

$$\boldsymbol{\Xi}^\top \mathbf{S}\boldsymbol{\Psi} = 0. \tag{5}$$

$\boldsymbol{\Psi}$ is the wavefunction eigenvector, E is the energy eigenvalue, $\mathbf{H}$ is the Hamiltonian matrix, $\mathbf{S}$ is the FEM mass matrix, and $\boldsymbol{\Xi}$ is the *adjoint state*. Supposing ψ is the groundstate wavefunction with energy E we may define the following squared-L_2 norm on the density, $\rho(x) = \psi(x)^2$, as the loss:

$$L[\rho(x)] = \int ((\rho_{target}(x) - \rho(x))/\epsilon)^2 dr, \tag{6}$$

where ϵ is a constant of normalization.

The discretized loss becomes:

$$\mathbf{L}[\mathbf{P}] = (\frac{\mathbf{P_{target}} - \mathbf{P}}{\epsilon})^\top (\frac{\mathbf{P_t} - \mathbf{P}}{\epsilon}). \tag{7}$$

Given that $\mathbf{P} = \boldsymbol{\Psi} \circ \boldsymbol{\Psi}$:

$$\overline{\boldsymbol{\Psi}} = -4 * (\frac{\mathbf{P_{target}} - \mathbf{P}}{\epsilon}) \circ (\frac{\boldsymbol{\Psi}}{\epsilon}) \tag{8}$$

With this each entry of $\overline{\mathbf{V}}$ can be computed and results in the newton iteration:

$$\mathbf{V}_{k+1} = \mathbf{V}_k - \overline{\mathbf{V}}_\mathbf{k}^+ \mathbf{L}[\mathbf{P}[\boldsymbol{\Psi}(\mathbf{V_k})]] \tag{9}$$

In the case of contributions from several wavefunctions the density $\mathbf{P}$ becomes:

$$\mathbf{P} = \sum_{j=0}^{M} \boldsymbol{\Psi}_\mathbf{j} \circ \boldsymbol{\Psi}_\mathbf{j} \tag{10}$$

The variation becomes the total variation and the entries of $\overline{\mathbf{V}}$ become:

$$\overline{\mathbf{V}} = \sum_{j=0}^{M} \overline{\mathbf{V}}_\mathbf{j}, \tag{11}$$

where j denotes the order and M denotes the highest eigenpair order (i.e. highest occupied orbitals).

III. Augmented Lagrangian Technique

Necessarily, inverse problems are computationally expensive with respect to the model they are optimizing on. As such, care must be taken in the design of the optimizer.

Since we are interested in optimizing a resource intensive model in high dimensions our options become limited. Zeroth-order techniques fail beyond intermediate dimensionality and second-order techniques become computationally costly as, without a sparse structure, any such optimizer will require dense matrix-vector multiplication in high dimensions.

Constraint requirements further limit our options.

We utilize the Augmented Lagrangian method as it is a first-order optimizer that incorporates constraints by approximating Lagrange multiplier updates with the penalty method [8].

Denoting f_t a particular target value as a function of the energy and $f(E)$ its current numerical value, we choose the constraint on the HOMO and total energies to be quadratic i.e. $(f(E) - f_t)^2$ and their penalties to be quartic i.e. $(f(E) - f_t)^4$. The corresponding adjoints for the total and ground state energies take the forms:

$$\overline{E}_{Total} = 2\lambda_{E_{Total}}((\Sigma_i E_i) - E_{Total}) + 2\mu((\Sigma_i E_i) - E_{Total})^3 \tag{12}$$

$$\overline{E}_{Homo} = 2\lambda_{E_{Homo}}(E_0 - E_{Homo}) + 2\mu(E_0 - E_{Homo})^3 \tag{13}$$

With the above adjoints, the contributions of the total and HOMO energy constraints and penalties to the overall Jacobian are:

$$\overline{\mathbf{V}}_\mathbf{Etot} = \overline{E}_{Total} * \sum_{j=0}^{M} \boldsymbol{\Psi}_\mathbf{j} \circ \boldsymbol{\Psi}_\mathbf{j} \tag{14}$$

$$\overline{\mathbf{V}}_\mathbf{Ehomo} = \overline{E}_{HOMO} * \boldsymbol{\Psi}_\mathbf{homo} \circ \boldsymbol{\Psi}_\mathbf{homo} \tag{15}$$

We note that more complex adjoints if needed can be computed using a matrix calculus CAS [9].

IV. The ADEXC Algorithm

The central problem in Density Functional Theory is the absence of an analytical form of the Exchange Correlation functional V_{XC} [1], [10]. Thus, numerical inaccuracy, and computational inefficiency, invariably arise from its application to extended systems as a result of the the functional's non-locality and approximate formulation.

We note that advanced quantum chemistry methods can recover more exact electron densities, but, as the V_{XC} functional lacks analytical form, these densities cannot elucidate the exchange-correlation. In this work, we argue there is in fact no need for an analytical form; by formulating an inverse DFT problem with respect to exact axillary calculations of observables, one can expect to recover the exact *numerical* value of the Exchange Correlation at each point in space. We note that all other IDFT algorithms that have been developed do not aim a reproducing an analytical result as well [11]–[13]. If the algorithm fails to converge in the case of a known analytic form, the problem is ill-conditioned Q.E.D.

Our proposed approach, ADEXC, in **Algorithm 1**, can then be seen as a *model-closure* algorithm. The only observables by which IDFT can be constrained are the density, the total ground state and HOMO energies. The precise difference between prior work and ADEXC is that in addition to the density objective the algorithm is further *spectrally constrained* by the HOMO and the ground state total energies to reduce the possibility of ill-conditioning at the level of the model itself.

Algorithm 1 ADEXC technique

1) Initialize tuple $[\mu, \lambda_{E_{Total}}, \lambda_{E_{HOMO}}]$
2) Initialize V_{XC}
3) Until convergence;
   - Compute the eigendecomposition, $H_{KS}[V_{XC}^k]\Psi(r) = E\Psi(r)$
   - Compute the variation, with respect to the wavefunction, of the density mismatch, for each wavefunction; $\overline{\psi}_i(r) = -4(\rho_{target}(r) - \rho[V_{XC}(r)])\psi_i(r)$
   - Solve the adjoint state equations for all eigenmodes; $(H_{KS}[V_{XC}^k] - E_i)\xi_i(r) = \overline{\psi}_i(r) - (\int \overline{\psi}_i(r)\psi_i(r)dr)\psi_i(r)$, subject to $\int \xi_i(r)\psi_i(r)dr = 0$
   - Compute Jacobian of density mismatch; $\frac{\delta||\rho_{target}(r)-\rho[V_{XC}(r)]||_2^2}{\delta V_{XC}(r)} = \Sigma_i \xi_i(r)\psi_i(r)$
   - Compute derivative of energy constraints and penalties, with respect to the spectrum; $\overline{E}_{Total} = 2\lambda_{E_{Total}}((\Sigma_i E_i) - E_{Total}) + 2\mu((\Sigma_i E_i) - E_{Total})^3$ $\overline{E}_{Homo} = 2\lambda_{E_{Homo}}(E_0 - E_{Homo}) + 2\mu(E_0 - E_{Homo})^3$
   - Compute Jacobians of energy constraints and penalty; $\overline{E}_{Total}\rho(r)$, $\overline{E}_{Homo}\psi_{Homo}(r)^2$
   - Compute Loss; $L = L_1 + L_2 + L_3$ with $L_1 = ||\rho_{target}(r) - \rho[V_{XC}(r)]||_2^2$ $L_2 = \lambda_{E_{Total}}((\Sigma_i E_i) - E_{Total})^2 + (\mu/2)((\Sigma_i E_i) - E_{Total})^4$ $L_3 = \lambda_{E_{Homo}}(E_0 - E_{Homo})^2 + (\mu/2)(E_0 - E_{Homo})^4$
   - Sum jacobians as $\frac{\delta L}{\delta V_{XC}^k}$; compute update (formally as) $V_{XC}^{k+1} = V_{XC}^k + L\frac{\frac{\delta L}{\delta V_{XC}^k}}{\int (\frac{\delta L}{\delta V_{XC}^k})^2 dr}$
4) $[\mu, \lambda_{E_{Total}}, \lambda_{E_{Homo}}] = [8\mu, \lambda_{E_{Total}} + \mu((E_0 - E_{Homo})^2), \lambda_{E_{Homo}} + \mu(((\Sigma_i E_i) - E_{Total})^2)]$
5) Go to 3 if V_{XC} did not converge yet.

V. Preliminary Results

We demonstrate the algorithm on **LiH** where we recover the LDA exchange-correlation from its resulting density. We run the algorithm for 512, 1024 and 2048 inner iterations within 16 outer iterations, initializing the exchange-correlation with the LDA exchange only. We note that the L_2 norms on the density exceeds benchmarks in [12]. Benchmarks for L_2 norms on the exchange-correlation with respect to LDA are introduced in this work.

We employ gradient descent with learning rate:

$$\gamma = \frac{\int (V_{XC}^k - V_{XC}^{k-1})(\frac{\delta L}{\delta V_{XC}^k} - \frac{\delta L}{\delta V_{XC}^{k-1}})dr}{\int (\frac{\delta L}{\delta V_{XC}^k} - \frac{\delta L}{\delta V_{XC}^{k-1}})^2 dr}, \qquad (16)$$

with a bisecting line-search backtracking on the inner iterations to enhance stability.

The penalty term is initialized to 10^{-3} and the penalty is updated by: $\mu \to 10\mu$, on the condition of divergence of either constraint at the end of each outer iteration. All computations are performed on FEM grids with quadratic approximation.

Figure 1 shows the history of all L_2 norms as well as relative errors on energy constraints.

As can be seen in Figures 1a and 1b density and exchange-correlation errors converge, improving with greater inner iterations; consistent with the convergence behavior of the Augmented-Lagrangian method.

Figures 1c and 1d demonstrate errors on the energy constraints. In the case of the HOMO energy, a figure of merit for these problems [11], the constraint converges for all inner iterations.

VI. Applications

The ADEXC algorithm is currently being tested and optimized on larger systems from molecules to small nanostructures.

Looking forward, we intend to extend this specific application to bandstructure calculations by recovering a localized potential from the IDFT procedure on a supercell [14].

Further, given a known exchange-correlation approximation such as LDA or GGA, that contribution can be fixed similar to the coulomb potential. In this scenario an external potential can be designed to reproduce any density configuration, such an external potential could implemented experimentally as a dopant profile or optical field, permitting a first-principles design of nanostructures [15].

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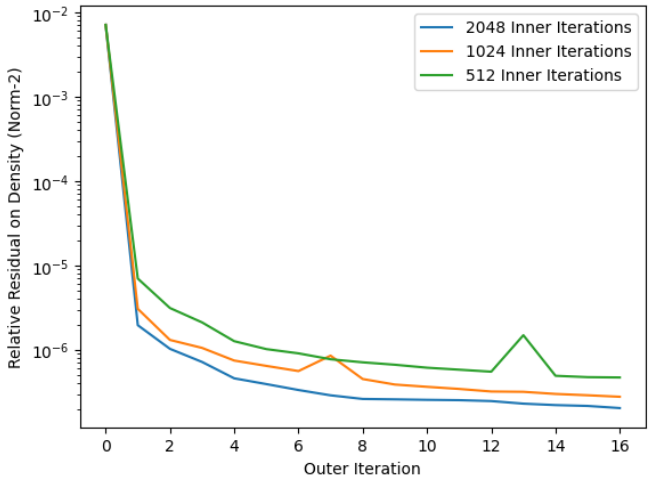
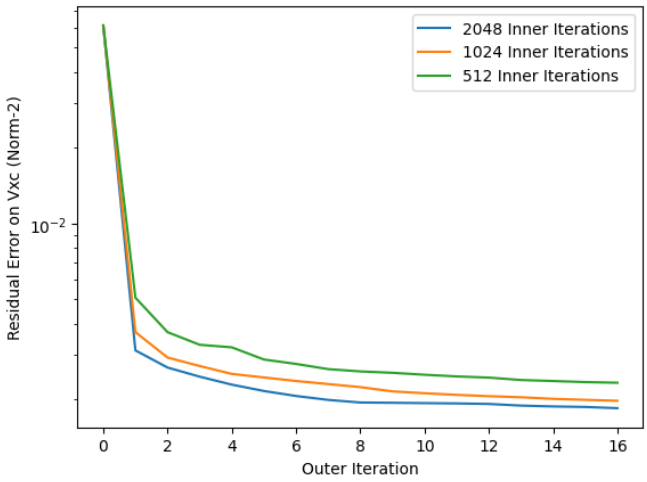
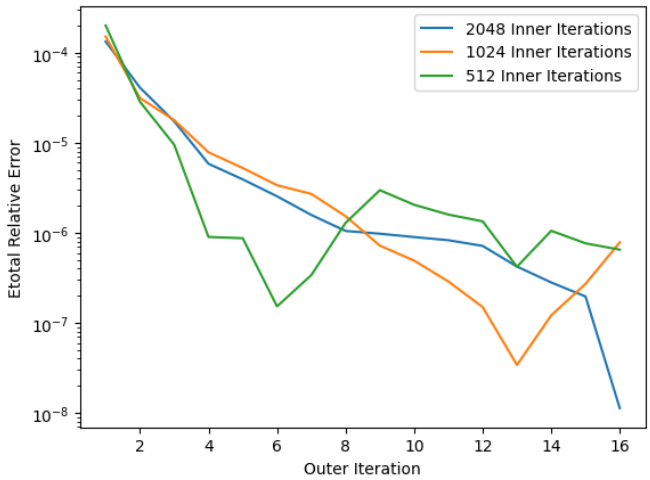


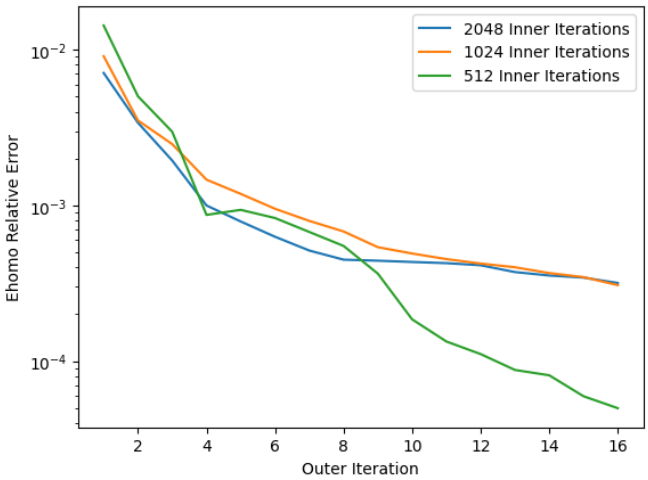
(a) Convergence of Density



(b) Convergence of V_{xc}



(c) Convergence of total energy



(d) Convergence of HOMO level

Fig. 1: Numerical Errors for **LiH** along the outer iterations, for different inner iterations, using gradient descent.

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