An Investigation Into the Mathematical Viability of On-the-Fly Optimization of the Hubbard Parameter in Approximate Density Functional Theory

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Abstract

Density functional theory is at the heart of many electronic configuration and total energy calculations computational physics and chemistry, and can be even be used in quantitative band-gap calculations[1]. The standard Local Density Approximation and Generalized Gradient Approximation approaches to constructing the correlation-functional for the total energy are relatively computationally inexpensive and yield accurate results in the many cases in which they are applicable.[2] Where they break down – in so-called 'strongly-correlated' systems – it is common to augment the model to the Hubbard model, adding a term dependent on the parameter U[3]. This parameter can be calculated using an involved procedure to measure linear-response properties of the system[4][5]. In this project, we present steps towards making the procedure more well-automated, by reframing the problem in terms of an extremization problem, and attempting to use results from cDFT and the standard DFT+U model to make the approach more numerically tractable for DFT codes such as ONETEP[6]. Calculations were done on two H_2^+ systems with interatomic separations of 2 and 6 a_0. In our calculations, an optimal Hubbard parameter of $U \approx 0.159$ eV for the first case and $U \approx 7.11$ for the latter. An extremization approach was developed by making assumptions about the linearity the first occupancy-derivative of subspace-averaged interaction potential as a function of U. Further research should be done to explore cases where this function may not be linear. Software tools were developed to make parsing of the data from the relevant calculations easier and to automate many of the steps needed in the linear-response approach.

I. Introduction

1. Density Functional Theory

Density functional theory (DFT) is an immensely powerful mathematical toolkit in computational physics and chemistry and is at the core of many large software packages for performing electron structure calculations on systems of many sizes, from simple atomic systems, to molecules, and even to crystalline solids.[7][8][9]

DFT relies heavily on the Hohenberg-Kohn theorems, which state that the total energy of a system may be described by functionals of the electron density function $n(\mathbf{r})$ alone.[10] Many approximations are required to make it possible to write the functional equations in a closed form, and more still are needed to make them tractable.

A key approximation in DFT is the Kohn-Sham approach, wherein a complicated interacting system of electrons is replaced by a non-interacting one with an equivalent ground-state energy.[11]

For an interacting system of electrons with wavefunctions ψ_i under an external potential v_{ext}, the ground-state energy is given by

$$E[n(\mathbf{r})] = T[n(\mathbf{r})] + V_{ee}[n(\mathbf{r})] + \int v_{\text{ext}}[n(\mathbf{r})]n(\mathbf{r})\text{d}\mathbf{r}, \quad (1)$$

where T is the kinetic energy and V_{ee} is the electron-electron repulsion energy.

Together, the first two terms comprise the universal function $F[n(\mathbf{r})]$. T is exactly given by

$$T = \sum_i^N k_i \left\langle \psi_i \left| -\frac{1}{2}\nabla^2 \right| \psi_i \right\rangle, \quad (2)$$

where k_i are occupancy numbers. For a non-interacting system with as many electrons, this becomes

$$T_s = \sum_i^N \left\langle \psi_i \left| -\frac{1}{2}\nabla^2 \right| \psi_i \right\rangle, \quad (3)$$

the Kohn-Sham energy. In this approach, $n(\mathbf{r})$ is given by

$$n(\mathbf{r}) = \sum_i^N |\psi_i(\mathbf{r})|^2 . \quad (4)$$

In this case, each ψ_i are the Kohn-Sham orbitals. The universal functional can then be written in terms of the Kohn-Sham energy as

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_{\text{Hartree}}[n(\mathbf{r})] + E_{\text{xc}}[n(\mathbf{r})]. \quad (5)$$

The Hartree energy $E_{\text{Hartree}}[n(\mathbf{r})]$ encodes the Coulombic interaction[12] in terms of $n(\mathbf{r})$ and is given by

$$E_{\text{Hartree}} = \frac{1}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\text{d}\mathbf{r}\,\text{d}\mathbf{r}', \quad (6)$$

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[1] (Parr and Yang 1989).
[2] (Perdew, Burke, and Ernzerhof 1996).
[3] (Anisimov, Aryasetiawan, and Lichtenstein 1997).
[4] (Coccioni and Gironcoli 2004).
[5] (Moynihan, Teobaldi, and O'Regan 2017).
[6] (Skylaris et al. 2005).
[7] (Parr and Yang 1989).
[8] (Skylaris et al. 2005).
[9] (Burke 2007).
[10] (Hohenberg and Kohn 1964).
[11] (Kohn and Sham 1965).
[12] (Parr and Yang 1989).

and E_{xc}, the *exchange-correlation* term, encodes the difference between the true and Kohn-sham kinetic energies, and the true electron-electron and Coulombic repulsion terms, *i.e.*

$$E_{\mathrm{xc}} = T - T_s + V_{ee} - E_{\mathrm{Hartree}}. \tag{7}$$

2. The Hubbard Correction

An exact, closed form of E_{xc} is not known[13]. A common, simple approximation is the Local Density Approximation (LDA) approach[14][15]. This approach usually assumes that the electrons are modelled by a homogeneous electron gas[16], and works well for a great many systems, but breaks down for strongly-correlated systems such as transition metals due to an intrinsic self-interaction error (SIE)[17][18]. In this case, amendments are made using the Hubbard model, which introduces new short-range interactions between electrons. A common term added to the exchange-correlation energy to implement this is

$$E_U = \frac{U}{2}\,\mathrm{Tr}\left(n - n^2\right), \tag{8}$$

which gives rise to the DFT+U formalism[19].

The traditional approach to obtaining the U parameter has been extrapolation from experimental data or other heuristic or empirical methods. In recent years a linear-response approach has been developed in order to calculate U *ab initio.*[20]

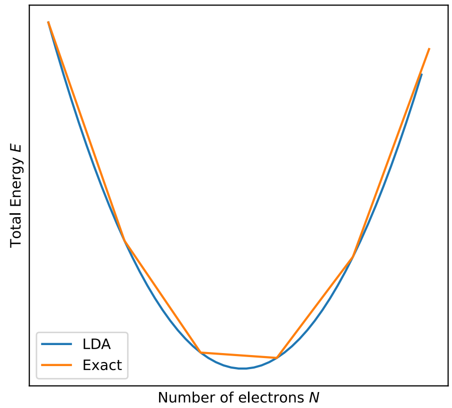

Fig. 1.1 The departure of LDA functionals such as PBE from experiment (and intuition) at fractional occupancies is a key failure the DFT+U formalism seeks to remedy[21][22]. Based on a figure from (Coccioni and Gironcoli 2004)

3. Constrained Density Functional Theory

Constrained density functional theory (cDFT)[23] is a method for imposing physical conditions, which is especially used for calculating excitation properties. Constraints on a system with density $n(\mathbf{r})$ and spin-states σ are of the form

$$C[n(\mathbf{r})] = \sum_{\sigma} \int w_c^{\sigma}(\mathbf{r}) n^{\sigma}(\mathbf{r})\,\mathrm{d}\mathbf{r} - N_c, \tag{9}$$

where N_c is a target electron number and w_c^{σ} is a projection operator. This is typically solved using the method of Lagrange multipliers, *i.e.* by building the functional

$$\mathcal{L} = E_{\mathrm{DFT}} + \alpha C, \tag{10}$$

and minimizing as outlined in the Kohn-Sham approach.

cDFT has been used to calculate a number of properties, including the U parameter[24].

4. Calculation of the U parameter using a linear response approach.

A recent method for calculating the U parameter from first principles is the linear response approach given by Moynihan, Teobaldi and O'Regan in Ref. (Moynihan, Teobaldi, and O'Regan 2017). One starts by performing a DFT calculation on a subspace of a system in its ground state, and then performing calculations on a number of perturbed states with perturbation strength α.

For that subspace, U is then given by

$$U = \left(\chi_0^{-1} - \chi^{-1}\right), \tag{11}$$

where χ is the interacting response function and χ_0 is the non-interacting Kohn-Sham response function, given as the total derivatives of the occupancy with respect to perturbation strength.

To make this system self-consistent, and thus to improve upon the calculated value of U, the subspace is first provided with an arbitrary input U-parameter U_{in} and the value of $f_{\mathrm{Hxc}}(U_{\mathrm{in}})$ calculated, where

$$f_{\mathrm{Hxc}} = \frac{\mathrm{d}v_{\mathrm{Hxc}}}{\mathrm{d}N} \tag{12}$$

is the subspace-averaged interaction potential (comprised of Hubbard and exchange-correlation popentials). Practically, f_{Hxc} can be found by perturbing the system fitting the computed potentials and occupancies to a curve using regression methods, and computing the first derivative of this function. Practically, $v_{\mathrm{Hxc}}(N)$ is usually linear, and so f_{Hxc} can be given as its slope. No universal analytical form of f_{Hxc} is yet known.

A successful self-consistency criterion is the $U^{(2)}$ regime outlined in (Moynihan, Teobaldi, and O'Regan 2017).

$$U_{\mathrm{out}} = f_{\mathrm{Hxc}}(U_{\mathrm{in}}) - U_{\mathrm{in}} = 0. \tag{13}$$

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[13] (Parr and Yang 1989).
[14] (Perdew, Burke, and Ernzerhof 1996).
[15] (Burke 2007).
[16] (Hohenberg and Kohn 1964).
[17] (Anisimov, Aryasetiawan, and Lichtenstein 1997).
[18] (Dudarev et al. 1998).
[19] (Dudarev et al. 1998).
[20] (Coccioni and Gironcoli 2004).
[21] (Anisimov, Aryasetiawan, and Lichtenstein 1997).
[22] (Coccioni and Gironcoli 2004).
[23] (O'Regan and Teobaldi 2016).
[24] (Coccioni and Gironcoli 2004).

To find a continuous form of $f_{\mathrm{Hxc}}(U_{\mathrm{in}})$ to find the optimal value of U that fulfills this criterion, a second regression must be performed. This method is thus cumbersome and prone to human error, and is not as well-automated as many density functional theory calculations.

In this report we investigate if it is possible to find a functional of the form (Eq. 10) which may be extremized in order to compute the U parameter using the well-tested, blackbox techniques associated with cDFT.

II. Methodology

1. The Dihydrogen Cation as a Testbed

The dihydrogen cation H_2^+ is a useful starting point for calculations. One can solve for the total energy of the system at any inter-atomic separation distance using the Born-Oppenheimer approximation[25], where the protons are considered as fixed in space and, importantly, its error is almost entirely due to SIE.

The DFT+U calculations needed to follow the method outlined in I-4 are supported by a range of DFT codes, including ONETEP, which has been employed throughout this investigation for performing the requisite calculations.[26][27]

Calculations were done on two systems with inter-atomic separations of 2 a_0 and 6 a_0, respectively. The former is considered a relatively small separation distance, whereas the latter is quite large, where the occupancy for each site should approach $N = 0.5$.

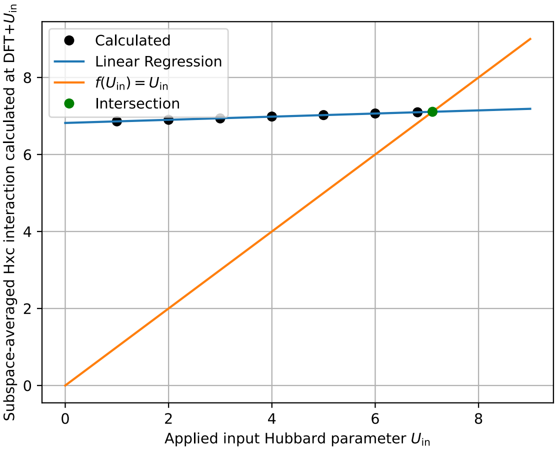

Fig. 2.1 The intersection of $f_{\mathrm{Hxc}}(U_{\mathrm{in}})$ and the identity function. The point of intersection is the value of U which fulfills the self-consistency criterion.

The converged values for total energy, subspace occupancies, as well as individual contributions from Hartree and exchange-correlation potentials were extrapolated from ONETEP output files and converted to `numpy` arrays. Occupancies n were taken from the results from unperturbed calculations at each step, here called n_0, for reasons justified in (III).

Linear regression was performed in Python using the `scipy` package. It is clear from Figure 2 that, at least in the case of H_2^+, $f_{\mathrm{Hxc}}(U_{\mathrm{in}})$ is very nearly linear, with Pearson r correlation coefficients close to 1 to within 5 significant figures for a range of U_{in} values between 1 and 10 eV.

The optimal value of U for the former system as given by the $U^{(2)}$ self-consistency scheme is $U_{\mathrm{opt}} \approx 0.159$. For the latter, it is $U_{\mathrm{opt}} \approx 7.11$.

2. A Naïve Approach to Enforcing the $U^{(2)}$ Self-Consistency Criterion as a Constraint

One possible, albeit naïve approach to finding an extremization-based approach to calculating the U parameter is by modelling the $U^{(2)}$ self-consistency formula $f_{\mathrm{Hxc}}(U_{\mathrm{in}}) - U_{\mathrm{in}} = 0$ as a constraint equation and solving using the method of Lagrange multipliers, *i.e.* by building the functional

$$\mathcal{L}_1[n,(U)] = E_{\mathrm{DFT}}[n] + \lambda\left(f(U) - U\right). \tag{14}$$

Unfortunately, this does not yield a useful result, as $\mathcal{L}$ can effectively be treated as a one-dimensional function of U, and the ultimate expression for λ, given by

$$\lambda = \frac{\frac{\partial E}{\partial U}}{1 - \frac{\partial f}{\partial U}}, \tag{15}$$

simply yields the trivial result $\partial E/\partial U = 0$.

3. Considering U as a Kind of Lagrange Multiplier for a System which Yields the Self-Consistency Criterion When Extremized

Another potential candidate for a functional $\mathcal{L}$ which might be used in an extremization procedure for finding U could be one in which U is thought of as a sort of Lagrange multiplier which is used to enforce the self-consistency constraint. Again, drawing from the approach in II.2, a functional can be constructed of the form

$$\mathcal{L}_2[n,(U)] = E_{\mathrm{DFT}+U}[n] + U^*\left(f_{\mathrm{Hxc}}(U) - U\right), \tag{16}$$

where $U^* = U/\left(1\text{ eV}\right)$. Note that we are here taking the total energy from the entire DFT+U calculation, which includes the energy given by

$$\frac{U_{\mathrm{in}}}{2}\,\mathrm{Tr}\left(n - n^2\right). \tag{17}$$

We will here consider the total derivative of $\mathcal{L}$ with respect to U.

One then has

$$\begin{aligned}\frac{\mathrm{d}\mathcal{L}}{\mathrm{d}U} &= \frac{\partial\mathcal{L}}{\partial U} + \frac{\delta\mathcal{L}}{\delta n}\frac{\mathrm{d}n}{\mathrm{d}U}\\ &= \frac{\partial E_{\mathrm{DFT}+U}}{\partial U} + \frac{\partial U^*}{\partial U}f_{\mathrm{Hxc}} + U^*\frac{\partial f_{\mathrm{Hxc}}}{\partial U} - \frac{\partial U^*}{\partial U}U\\ &\quad - \frac{\partial U}{\partial U}U^* + \frac{\delta\mathcal{L}}{\delta n}\frac{\mathrm{d}n}{\mathrm{d}U}.\end{aligned} \tag{18}$$

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[25] (Burrau 1927).

[26] (Skylaris et al. 2005).

[27] (Dziedzic et al. 2020).

One can use a result from cDFT[28] to show that, at the ground-state n_0, $\partial \mathcal{L}/\partial n = 0$. Thus,

The minimization then enforces

$$0 = \frac{1}{2}\left(n - n^2\right) + f^*_{\mathrm{Hxc}} + U^* \frac{\partial f_{\mathrm{Hxc}}}{\partial U} - 2U^*. \tag{19}$$

The asterisk again denotes non-dimensionalization. This result initially appears unuseful. In fact, it yields a U value serendipitously close to exactly half of that needed for the case of the dimer of larger bond length, as will be elaborated in (III). Note that this motivates a method by which to cancel the n-dependent term. This method is also hindered by its reliance on a closed form of f_{Hxc}.

4. Considering a Taylor Expansion-based Function which Yields the Optimal Hubbard Parameter when Extremized

Following from above, we put forward a reverse-engineering approach by beginning with the self-consistency criterion and noting that, within small energy intervals, $f_{\mathrm{Hxc}}(U_{\mathrm{in}})$ appears linear. The Taylor series expansion of f_{Hxc} based on an initial guess of $U_{\mathrm{in}} = U_0$ can be given as

$$f_{\mathrm{Hxc}}(U) = f_{\mathrm{Hxc}}(U_0) + (U - U_0)\frac{\partial f_{\mathrm{Hxc}}}{\partial U}|_{U_0}. \tag{20}$$

One can then take the anti-derivative of the self-consistency criterion to obtain the function

$$W(U,[n]) = \frac{U}{2}\left(U - 2f_{\mathrm{Hxc}}(U_0) - \left(f_{\mathrm{Hxc}}(U) - f_{\mathrm{Hxc}}(U_0)\right)\left(\frac{U - 2U_0}{U - U_0}\right)\right). \tag{21}$$

In order to create a functional of the form (Eq. 10) we may add this term to the total energy, with an added term to correct for the n-dependent energy derivative, thus constructing

$$\begin{aligned}\mathcal{L}_3(U,[n]) = {} & E_{\mathrm{DFT}+U}(U,[n]) + \\ & \frac{U}{2}\Bigg(U - 2f_{\mathrm{Hxc}}(U_0) - \\ & \left(f_{\mathrm{Hxc}}(U) - f_{\mathrm{Hxc}}(U_0)\right)\left(\frac{U - 2U_0}{U - U_0}\right) + 2\,\mathrm{Tr}\left(n_0 - n_0^2\right)\Bigg).\end{aligned} \tag{22}$$

The factor of 2 before the n_0-dependent term encodes the fact that the Hubbard approximation is applied to both sites of the dication. Note also that care must be taken to avoid errors in extremization due to the discontinuity at $U = U_0$. In principle, $\mathcal{L}$ will be exactly minimized at the optimal U value, and requires that a numerical value for $f_{\mathrm{Hxc}}(U)$ be found at only two values of U_{in}. Its exact utility will be discussed in (III). Whether results from cDFT can be used with this expression is unlikely, as it has been shown that cDFT is incompatible with non-linear constraints such as the one modelled here.[29]

III. Results

1. Verification of Linear Response of Subspace-Average Hartree Exchange-Correlation Potential as a Function of Occupancy N to an Input Hubbard Parameter U_{in}

For a small, non-crystalline calculation, the calculation cell in ONETEP is made appreciably larger than the total bond length. In all calculations, a standard, publically available, `recpot`-formatted pseudopotential for the hydrogen species was used to mitigate repetitive and resource-intensive calculations.

Data was aggregated from each separate perturbed calculation and formatted into `numpy`-compatible arrays using a shell script (see Appendix A).

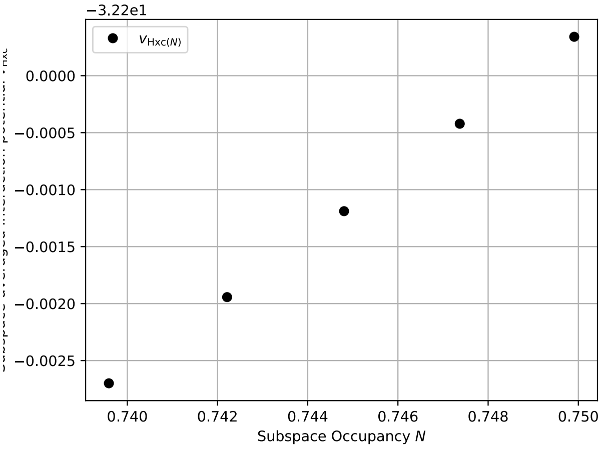

Fig. 3.1. Subspace-average Hartree exchange-correlation potential as a function of occupancy for a sample input U_{in} of 1 eV for the dimer of length 2 a_0. Note that this is nearly linear and that its slope is the numerically-evaluated form f_{Hxc}(1 eV).

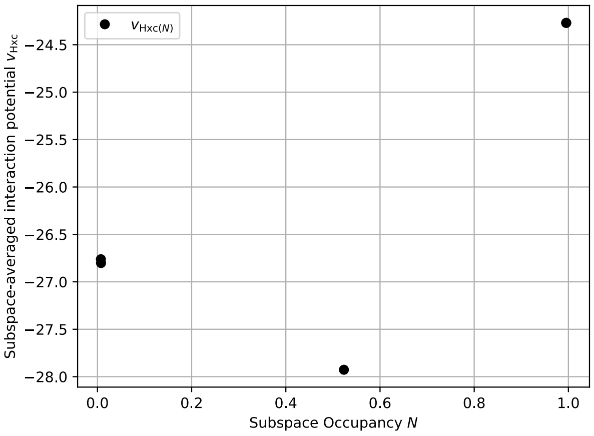

Fig. 3.2. Subspace-average Hartree exchange-correlation potential as a function of occupancy for a sample input U_{in} of 7 eV for the dimer of length 6 a_0. Here, due to large bond length, the response property becomes unusable due to symmetry breaking – note totally filled and totally empty orbitals.

Figure 3.2 indicates the limited range for inputted U parameters, since the system breaks down past approximated

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[28] (O'Regan and Teobaldi 2016).

[29] (Moynihan, Teobaldi, and O'Regan 2016).

7eV in the 6 a_0 case. This was not a problem for the much smaller dimer. Linear regression was used for each non-symmetry-broken step in order to find a continuous form of $f_{\mathrm{Hxc}}(U)$.

2. Calculation of Optimal Hubbard Parameter by Direct Solvation of Fixed Points of f_{Hxc}

Directly solving the self-consistency criterion is best achieved by performing another linear regression on the dataset and solving for the fixed point U^*, given by

$$U^* = \frac{c}{1-m}, \tag{23}$$

where c and m are the intercept and slope of the regression line, respectively.

Figures 3.3 and 2.1 show the individual numerical values of f_{Hxc} as a function of U alongside a linear interpolation for the 2 a_0 and 6 a_0 cases, respectively.

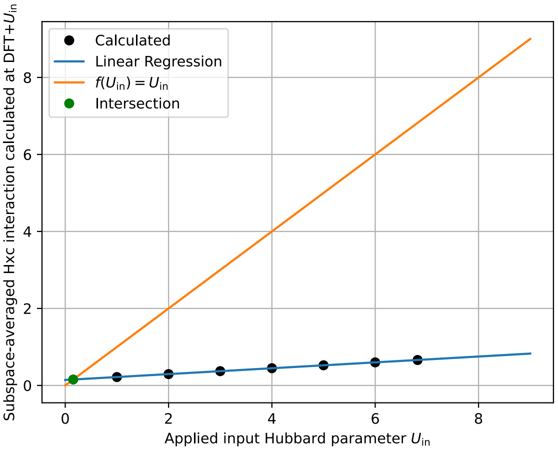

Fig. 3.3. The calculated f_{Hxc} values, their linear regression line, the identity function $f(U) = U$ and their intersection U^* for a continuous range of U.

An interesting result from these calculations is the optimized value of 7.11 eV for the 6 a_0 case, in contrast to the value of approximately 8 eV recommended by (Moynihan, Teobaldi, and O'Regan 2017).

3. Comparison of Directly-Solved Parameter to that Given by the $\mathcal{L}_2$ Functional

Extremization of $\mathcal{L}_2$ with respect to U was done using the optimization feature of `scipy`, although can in principle be done by extremization algorithms implemented in standard DFT(+U) codes[30].

In the 2 a_0 case, the extremized value was $U \approx 0.18$, which deviates from the directly-derived $U_{\mathrm{opt}}/2$ by more than 12%.

In the 6 a_0 case, the extremized value was $U \approx 3.68$, accurate to $U_{\mathrm{opt}}/2$ to within 3%.

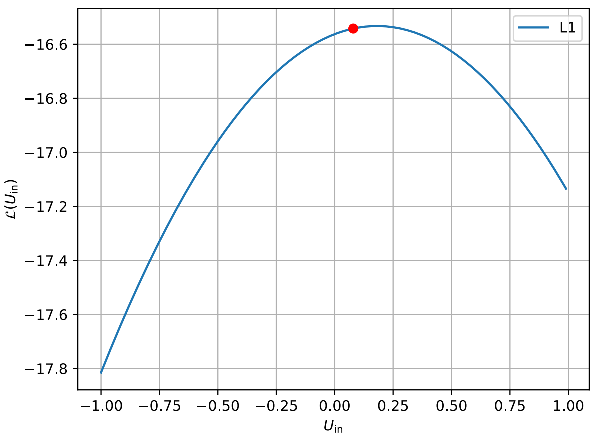

Fig. 3.4. Extremized $\mathcal{L}_2$ functional for the 2 a_0 case. The red spot highlights the analytical $U_{\mathrm{opt}}/2$.

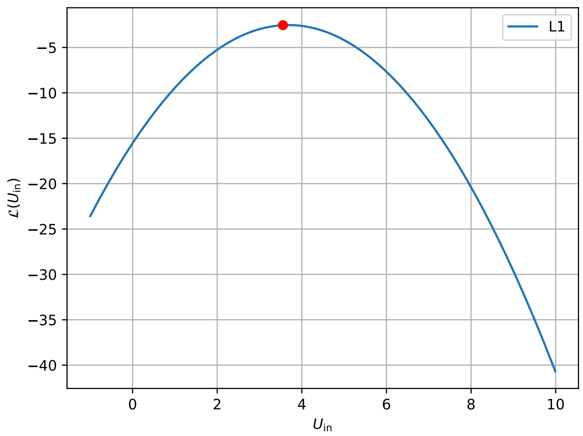

Fig. 3.5. Extremized $\mathcal{L}_2$ functional for the 6 a_0 case. Note proximity of $U_{\mathrm{opt}}/2$ to true maximum.

In both cases, the error is to in the second significant figure, illustrated by Figures 3.4 and 3.5. In practical applications of the functional (Eq. 8), an error of this scale is largely unimportant. While the drawbacks of this naïve approach have been discussed in (II), this investigation validates important approximations which may be extended to more complex systems.

4. Comparison of Directly-Solved Parameter to that Given by the $\mathcal{L}_3$ Functional

The $\mathcal{L}_3$ functional was implemented in Python with an ability to input some initial guess U_0 by which to compute the optimal U by finite differences. Rather than use the computationally expensive linear regression process used in the previous procedure, the value of $f_{\mathrm{Hxc}}(U_0)$ is drawn from the corresponding entry in the pre-computed array from the ONETEP output.

To verify correct implementation and analysis, $\mathcal{L}_2$ was plotted continuously, based on the linear regression computed in (III.2). For the 2 a_0 case, a minimum of -16.58 was found at the value of $U \approx 0.156$, for an initial guess $U_0 = 6$ eV and with an approximate n_0 of 0.75. This is within 2.5% of the desired value, with accuracy relying mostly on the the value of n_0 used. For the 6 a_0 case, a minimum of -39.76 was found at the value of $U \approx 7.11$ with the same initial guess and approximate n_0 of 0.52.

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[30] (Dziedzic et al. 2020).

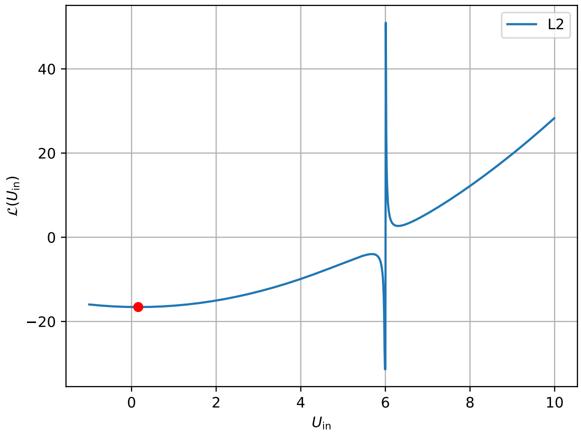

Fig. 3.6. $\mathcal{L}_2$ over a continuous range of U_{in} for the initial guess of 6 eV, for the 2 a_0 case. Note the discontinuity at the guess.

Having verified this analysis, we look at the case where $\mathcal{L}_2$ is known only at explicitly-calculated values of f_{Hxc}. Here, the minimization procedure is drastically simplified, at the expense of accuracy: we need only look at the index of minimum of the array of computed $\mathcal{L}_2$ values (taking analytic discontinuity into account), and take the value of the array of U_{in} values corresponding to this index. This procedure may be done for a number of guesses, and an average taken.

Figure 3.7 shows an important limitation which emerges as a result of the symmetry-breaking phenomenon seen after a U_{in} of approximately 7 eV. Here, no value in the array exceeds the needed value, curtailing the range in which we may look for the minimum.

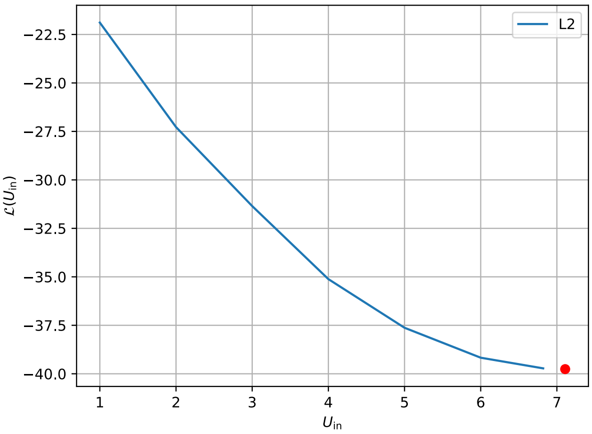

Fig. 3.7. $\mathcal{L}_2$ over a continuous range of U_{in} for the initial guess of 2 eV, for the 6 a_0 case. Note that the desired value is outside of the computable range.

In this case, it is fortunate that the value found using the rounding-and-averaging scheme above corresponds to one that might be found over a broader range, but this approach should be treated with caution for systems where this may not be the case.

IV. Conclusion

This project has put forth a method by which to compute an optimal Hubbard U parameter for a many-body quantum-mechanical system using an extremization method which derives from the self-consistent field linear response approach. In our calculations, the parameter has been explicitly computed for two simple H_2^+ systems with respective interatomic separations of 2 and 6 Bohr radii. Of three approaches tried, the initial approach, constraining the system with the self-consistency criterion and using results from cDFT, was shown to render only trivial results; the second approach illuminated approximations which might be made but was on the whole inaccurate, while the third approach was broadly the most successful, effectively supplanting a linear regression step with an extremization step in the computational process. The method was shown to have various limitations, including the assumption that the subspace-averaged interaction potential as a functional of U is linear in a region around some initial guess U, and its accuracy is inherently limited by the granularity of inputted U parameters used in calculations. The method may also depart from the proposition to create an optimization method compatible with results from cDFT.[31]

A number of software utilities were developed to aid in the parsing of results from ONETEP calculations and in the computation of the U parameter using both the standard and extremization-based linear response approaches.

The efficacy of the method in more complex systems – particularly systems such as transition metals, where the Hubbard correction is most essential – is yet to be explored. Complications may arise in the approximations used to correct for the U-dependence in the total energy computed in standard DFT+U, especially considering that the number of sites must be taken into account in the Dudarev-correcting term.

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[31] (Moynihan, Teobaldi, and O'Regan 2016).

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