The self-interaction correction in the time domain

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Abstract. We provide a brief outline of the Self Interaction Correction (SIC) used in connection with the Local Density Approximation (LDA) of Density Functional Theory (DFT), pointing out especially the implications for Time Dependent theories (TDDFT). We discuss how the self-interaction problem can be resolved by a clean formulation of the SIC theory including in an explicit manner the ortho-normalization of Kohn Sham orbitals. We finally show a few examples of applications of the theory.

1. Introduction

The dynamics of finite Fermion systems under strong perturbations has focused numerous investigations, in many domains of physics, ranging from electronic dynamics, especially in clusters [1] and plasma physics [2] to nuclear collisions [3]. From the theoretical point of view the problem is still far from being solved. Several difficulties remain, both at the formal and practical levels. The formulation of well founded theories for the SIC thus remains a key issue. The practical goal of our investigations is specifically to study the dynamics of clusters and molecules subject to an irradiation by a laser or a charged projectile. We aim at providing a fully dynamical description of such processes including electron and ion dynamics, as well as possible response of the environment when present (as e.g. in the case of solvated molecules [4] or embedded/deposited clusters [5, 6]). We furthermore require a high degree of accuracy especially at low energy, as we aim, in particular, to analyze phenomena close to ionization thresholds.

Density Functional Theory (DFT) [7], extended in the time domain (Time Dependent DFT = TDDFT) [8], appears here as a most promising theory for addressing such questions. DFT provides a major tool of investigation in numerous physical and chemical systems since several decades, both for static and dynamical problems. It now constitutes a well founded theoretical basis on which to develop elaborate approaches. It, nevertheless, still raises numerous formal difficulties. We shall address here the specific well known pathology of the self-interaction error which is non-ignorable in the dynamical description of irradiation processes which usually involve electronic emission.

The simplest approximation to DFT is the well known Local Density Approximation (LDA). It provides a simple ansatz to account for exchange and correlation on the basis of a Fermi Gas approximation. It constitutes an extremely useful tool in DFT because of its simplicity and robustness. The LDA approximation furthermore provides a most sound basis for many theoretical developments. But it suffers from a self-interaction error: one electron interacts with
the mean-field, itself a functional of the total density (hence including this one electron itself). Each electron thus spuriously interacts with itself. This pathology, typical of Hartree mean-field, is explicitly cured by the exchange term in the Hartree-Fock approximation. The approximate LDA exchange nevertheless does not suffice to restore a proper cancellation, which leads to a spurious residual self interaction. This defect can unfortunately have sizable consequences, especially on ionization properties (Ionization Potential (IP) in particular), which is catastrophic for the description of irradiation processes. The aim of this contribution is to discuss strategies to cure this defect by a Self-Interaction Correction (SIC) in a truly dynamical context compulsory for a proper description of irradiation dynamics.

The paper is organized as follows. After a brief introduction to DFT and LDA we illustrate the self-interaction problem on a typical example. We then introduce standard SIC approaches, explain their limitations and the need for improved formulations. We finally present a recently introduced clean formulation of SIC and illustrate the improvement it brings on typical examples.

2. From DFT to LDA
There exist many well documented presentations of DFT, LDA and TDDFT. We refer the reader to these various references for more details [7, 8] restrict the present discussion to a brief introduction of DFT and LDA as basis for the further discussion. The considerations are restricted to electrons here, ions being treated as classical particles all over. We work in the Kohn-Sham [9] scheme of DFT in which the system is represented by a set \( \{ \psi_\alpha, \alpha = 1, \ldots \} \) of single-electron wave functions. From them one constructs the one-body density, \( \rho = \sum_\alpha |\psi_\alpha|^2 = \sum_\alpha \rho_\alpha \), which is the key ingredient of DFT according to Hohenberg and Kohn’s theorem [10]. The resulting theory involves a single-electron Hamiltonian, \( h[\rho] = h_0 + U_H + U_{xc} \), where \( h_0 = -\frac{\hbar^2}{2m} \Delta \) is the kinetic term and \( U_H \) the Hartree (direct) Coulomb interaction. The exchange correlation term, \( U_{xc} \), is a functional of the density \( \rho(r) \), which has to be properly chosen.

The Local Density Approximation (LDA) provides the simplest approximation for \( U_{xc} \) and consists in assuming the system as infinite and homogeneous to compute this term, locally. This amounts to replace \( U_{xc}[\rho^\infty] \) by \( U_{xc}[\rho(r)] \), where \( \rho(r) \) is the local density and \( \rho^\infty \) the density of the corresponding infinite system with homogeneous density \( \rho(r) \). The exchange correlation term thus becomes a simple function of the local density \( \rho(r) \). We denote by \( U_{LDA} \) the corresponding one-body potential \( (U_{LDA} = U_H + U_{xc}) \). By construction, LDA should be valid only for systems in which the density \( \rho(r) \) varies sufficiently slowly. In fact, it performs usually much better than expected. It can thus be successfully applied to situations with non-vanishing density gradients and it thus constitutes a sound basis for the construction of more elaborate approximation schemes.

3. The SIC problem
In spite of its many successes, LDA suffers from the self interaction problem since the approximate exchange term does not cancel exactly the self interaction contribution in the direct term. This is a key issue in electronic systems in which Coulomb exchange provides a very large fraction (typically 3/4) of the total binding of a system. A poor treatment of the self interaction then necessarily leads to measurable pathologies. The simplest example is provided by the IP which sensitively depends on the self interaction. Indeed the LDA approximation exhibits a wrong asymptotic behavior of the electronic potential: a departing electron does not feel the correct potential due to electrons remaining in the system. This causes an incorrect value of the IP when estimated from the Highest Occupied Molecular Orbital (HOMO), which reflects a violation of Koopmann’s theorem [11]. Although acceptable in a purely static context, this defect becomes dramatic in a truly dynamical situation in which one wants to follow ionization "on the fly".
Figure 1 shows IP's in the case of a sequence of carbon cycles, in which carbon atoms are replaced by nitrogen or oxygen atoms. In the whole sequence of test cases the effect is the same: a strong underestimation of the IP, with a relative error of order 50%. As will be clear below this defect reflects the absence of SIC in LDA which thus badly fails.

4. Self Interaction Correction (SIC) and Optimized Effective Potential (OEP)

4.1. Basics of SIC-OEP

The basic SIC method was introduced in the late 1970's and consists in subtracting "by hand" the spurious self interaction [13]. This amounts to define a total SIC energy $E_{\text{SIC}}$ and the corresponding one-body Hamiltonian, obtained from variation of $E_{\text{SIC}}$ with respect to $\psi_\alpha^*$, as

$$E_{\text{SIC}} = E_{\text{LDA}}[\rho] - \sum_{\beta=1}^{N} E_{\text{LDA}}[|\psi_\beta|^2], \quad (1)$$

$$h_{\text{SIC,}\alpha} = h_{\text{LDA}} - U_{\text{LDA}}[|\psi_\alpha|^2] = h_0 + U_{\text{SIC,}\alpha}, \quad (2)$$

where $U_{\text{SIC,}\alpha} = U_{\text{LDA}}[\rho] - U_{\text{LDA}}[\rho_\alpha]$. A problem is here that the resulting one-body Hamiltonian does depend on the orbital on which it acts which, in turn, has inconvenient consequences. The orbital dependence a priori breaks the ortho-normality of the $\psi_\alpha$, which may severely plague any time dependent SIC calculations, if formulated that way. This ortho-normality problem is well known since the early days of SIC methods and several strategies have been developed to circumvent it, in particular in the stationary case.

A standard way out is to construct an approximate single one-body Hamiltonian common to all orbitals. This approach relies on a general method to do so, applicable to any mean-field theory (such as Hartree Fock in particular) and which is known as the Optimized Effective Potential (OEP) [14], having been introduced much earlier than SIC. The idea beyond is remarkably simple and elegant. It first consists in parameterizing the single-particle orbitals $\varphi_i^{V_0}$ by a common (optimal) potential $V_0$ (yet to be constructed). We introduce purposely a new notation in order to properly distinguish these orbitals from the original $\psi_\alpha$ wave functions, which by construction belong to a more general Hamiltonian. One then writes down the total energy (Hartree-Fock, SIC, . . .) using these parameterized wave functions as single electron orbitals. There remains to construct the potential $V_0$ itself. This is achieved by optimizing the total energy with respect to the potential $V_0$, which first provides $V_0$. From $V_0$ one then obtains the associated wave functions $\varphi_i^{V_0}$. The problem has then been solved, in a variational manner,
but in a restricted Hilbert space, ”parameterized” by \( V_0 \), which by construction is a potential common to all orbitals.

In the SIC case one can formally summarize the SIC-OEP procedure by:

\[
\begin{align*}
    \hbar_{\text{OEP}} \, |\varphi_i^{V_0}\rangle &= (\hbar_0 + V_0) |\varphi_i^{V_0}\rangle = \epsilon_i |\varphi_i^{V_0}\rangle, \\
    E_{\text{OEP}} &= E_{\text{SIC}}[\{\varphi_i^{V_0}\}], \\
    \frac{\delta E_{\text{OEP}}}{\delta V_0} &= 0 \rightarrow V_0 \rightarrow \varphi_i^{V_0}.
\end{align*}
\]

One can furthermore separate \( V_0 \) into 3 components (associated to various degrees of approximations) : \( V_0 = V_S + V_K + V_C \). The first term \( V_S \) corresponds to the simplest Slater approximation [16], the complementing term \( V_K \) associated to \( V_S \) provides the well known KLI approximation \((V_S + V_K)\) [17] and finally \( V_C \) is a correction usually assumed small. One can derive explicit expressions for these various terms, but most calculations have been performed at Slater or KLI levels, the full OEP-SIC equations being in most cases extremely demanding to solve in practical cases [15]. We write down for illustration the (simple) Slater term:

\[
V_S = \sum_i \frac{|\varphi_i^{V_0}|^2}{\rho} U_{\text{LDA},i},
\]

where \( U_{\text{LDA},i} = U_{\text{LDA}}[|\varphi_i^{V_0}|^2] = U_{\text{LDA}}[\rho_i] \) which nicely shows the average (over single electron orbitals) character of the produced OEP. The Slater approximation can be further simplified to provide the Average Density SIC (ADSIC) [18] by making the replacement \( \rho_i \rightarrow \rho/N \) (where \( N \) is the total number of electrons in the system). This particularly simple ADSIC approximation has been successfully applied to metal clusters [18] and organic systems [12]. This is illustrated in figure 1 where it can be seen that ADSIC provides a very good reproduction of carbon cycle IP’s: it remarkably solves the IP problem and restores Koopmann’s theorem.

### 4.2 Limitations

In spite of their successes, neither ADSIC nor the more involved Slater or KLI approximations are fully satisfying. The potential energy surface of \( C_2 \), as shown in figure 2, demonstrates one of the problems. ADSIC is totally off at large distances while Slater and KLI show a strange bump at intermediate distances. This bump spoils dissociation properties, a key issue when considering...
irradiation processes. It reflects a "conflict" at the side of single-electron wave functions, namely the fact that in this transitional range single electron orbitals have to find a compromise between localization (asymptotic configuration) and delocalization (molecular state).

The case of the dynamical evolution of Na\textsubscript{5} presented in figure 3 is even more dramatic. The total energy is plotted as a function of time and found to be badly violated in a standard Slater calculation. This defect can be proven analytically. It is then found that energy and zero force theorem are explicitly violated in time, in Slater and KLI approximations [19].

These pathologies call for an improvement of SIC approaches, both in its full and OEP approximate versions. This is what will be discussed in the following section.

5. SIC revisited
5.1. Time Dependent SIC
As noted above, the basic primary defect of the original SIC formulation is the lack of a proper ortho-normalization of single-electron orbitals. A simple cure is to enforce ortho-normalization within the variational principle itself, by introducing a set of Lagrange parameters $\lambda_{\beta\alpha}$. The variational principle then reads

$$\delta \psi_{\alpha}^{\ast} (E_{\text{SIC}} - \sum_{\beta,\gamma} (\psi_{\beta} | \psi_{\gamma}) \lambda_{\gamma\beta}) = 0 \quad (7)$$

which leads to the set of coupled equations

$$h_{\text{SIC},\alpha} | \psi_{\alpha} \rangle = \sum_{\beta} \lambda_{\beta\alpha} | \psi_{\beta} \rangle, \quad (8)$$

$$0 = (\psi_{\beta} | U_{\text{LDA}} [\rho_{\beta}] - U_{\text{LDA}} [\rho_{\alpha}] | \psi_{\alpha}) \quad (9)$$

The second equation, called "symmetry condition", stems from the ortho-normality constraint and becomes a crucial ingredient of the theory. Thanks to the variational formulation, there necessarily exists a solution to this set of equations. The enforcement of ortho-normalization in SIC was already proposed some times ago in static calculations [20, 21]. Very recently, the formalism was extended to the time domain [22, 23]. We briefly outline it below.

Starting point is the quantum action including explicit ortho-normalization and on which variational principle is applied

$$0 = \delta \int_{t_0}^{t} dt' (E_{\text{SIC}} - \sum_{\alpha} (\psi_{\alpha} | i\hbar \partial_{t} | \psi_{\alpha}) - \sum_{\beta,\gamma} (\psi_{\beta} | \psi_{\gamma}) \lambda_{\gamma\beta}) \quad (10)$$

This leads to

$$(\hat{h}_{\alpha} - i\hbar \partial_{t} ) | \psi_{\alpha} \rangle = \sum_{\beta} | \psi_{\beta} \rangle \lambda_{\beta\alpha} \quad (11)$$

Figure 3. Time evolution of the total energy of ground state Na\textsubscript{5} cluster in various approximations as indicated. Two time steps have been used in the Slater case and led to results exactly superimposing each other.
to be complemented again by the symmetry condition (9). The difficult point is now to propagate single electron orbitals. Indeed the Lagrange multipliers imply a non-trivial propagation scheme as they are explicitly time dependent. A way out is to introduce two sets of single electron wave functions. The idea behind the double set strategy is to exploit a degree of freedom which is usually neglected in DFT. One can perform any unitary transformation among the occupied single-electron orbitals without changing the total Slater determinant. In practice, we introduce two sets of single-electron orbitals linked by such an unitary transformation. The first set \( \{\psi_\alpha\} \) (as introduced above) serves to fulfill the symmetry condition (9). It turns out that it provides usually well localized wave functions. The second set \( \{\varphi_i\} \) serves to diagonalize the SIC Hamiltonian, Eq. (8). Then, the single electron equations of motion become

\[
(\hat{h}_{\text{SIC}} - i\hbar \partial_t) |\varphi_i) = 0
\]

which can be solved with standard time propagation

\[
|\varphi(t)\rangle = e^{-i \int_{t_0}^{t} dt' \hat{h}_{\text{SIC}} / \hbar} |\varphi(t_0)\rangle
\]

which resolves the propagation puzzle. In practice, we propagate the two sets of wave functions simultaneously, the \( \{\varphi_i\} \) are determined from time evolution (13) and the unitary transformation to the \( \{\psi_\alpha\} \) is determined at each time step to fulfill the symmetry condition (9). Note also that the SIC Hamiltonian is constructed from the \( \{\psi_\alpha\} \) orbitals.

The capability of this new Time Dependent SIC (TDSIC) formulation is illustrated in figure 4, in which we compare a TDSIC calculation with Time Dependent Hartree Fock (TDHF) and LDA. Calculations have been performed in the exchange only approximation such that TDHF becomes exact in that case and thus provides a simple benchmark. As can be seen from the figure TDSIC fully matches TDHF leading to exactly the same ionization after an initial perturbation. In turn, the LDA calculation leads to a much larger ionization due to the significantly higher IP in that case. Note however that the TDSIC is numerically expensive and this calls for further approximations.

5.2. Generalized OEP and Slater

The double set strategy also provides a means to reformulate the OEP approach so that one can re-derive Slater-like and KLI-like approximations in a much better justified manner and thus with a larger range of applicability. One intuitively sees that the \( \{\varphi_i\} \) are probably structurally close to the SIC-OEP \( \varphi_{iV_0} \) wave functions. This actually provides the basis for the development of the so called the Generalized Slater (GSlat) approximation [24] which can be formulated both
in a static and a dynamical context [25]. Because of the localization of the \( \{ \psi_\alpha \} \) wave functions, one can demonstrate that the usual Slater approximation becomes more accurate, provided the potential is expressed in terms of the \( \{ \psi_\alpha \} \). The OEP problem, in turn, remains solved at the level of the \( \varphi_i V_0 \) wave functions. This formally reads

\[
\begin{align*}
\hbar \Omega_{\text{EOP}} | \varphi_i V_0 \rangle &= \varepsilon_i | \varphi_i V_0 \rangle, \\
V_0 \simeq V_{\text{GSlat}} &= \sum_\alpha \frac{|\psi_\alpha|^2}{\rho} U_{\text{LDA}} |\psi_\alpha|^2,
\end{align*}
\]

(14)

(15)

with both sets connected by the proper unitary transform. In its stationary version, GSlat provides results extremely close to the full SIC ones. For example, it restores dissociation properties of \( \text{C}_2 \) (figure 2). It also provides improved values of polarizabilities as compared to Slater [26]. Time-Dependent GSlat also constitutes a better approximation than the mere Slater. Still, the formal shortcomings of Slater (energy and ZFT violations) are not strictly cured formally. The onset of the instability is merely postponed. This has, nevertheless, the interesting consequence that TDGSlat can be used for spectral analysis in the linear regime, while Slater cannot. The point is illustrated in figure 5 where total energy and dipole momentum of a small quantum dot (containing 6 electrons) are plotted as a function of time for various schemes.

6. Conclusions

We have discussed in this paper the self-interaction problem in finite electronic systems, especially from a dynamical point of view. We have proposed an improved scheme for solving several of the original SIC pathologies. The self interaction problem is a well known defect of LDA and stems from the fact that exchange is treated in an approximate manner in LDA. In spite of the successes of LDA it is in particular unable to properly describe ionization properties because of this self interaction problem. This has dramatic consequences on the description of dynamical scenarios in irradiation processes. The SIC method is supposed to cure this problem.
But it also suffers from pathologies linked in particular to the loss of ortho-normalization of wave functions by construction. The OEP method, in conjunction with SIC, allows to derive a formally clean approximate theory to full SIC, but produces extremely involved equations. The simplest approximations, Slater and KLI, although being used frequently, still suffer from severe defects, both formally and practically. We have thus proposed to revisit the SIC problem by reformulating the theory with explicit ortho-normalization. We have, furthermore, developed a two set strategy which is practically compulsory in the time domain, but which also exhibits interesting properties in the static case. It allows, for example, to derive an extension of the Slater approximation, the Generalized Slater approximation, which provides an interesting a wider range of applicability in statics and in the linear domain of dynamics. Nevertheless, the ultimate approach still remains the full TDSIC and it would be extremely valuable to optimize it further from a numerical point of view in order to apply it to large realistic systems in a truly dynamical context.

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