Time-dependent Generalized SIC-OEP formalism and Generalized SIC-Slater approximation.

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We propose a simplification of the full “2 sets” Time dependent Self Interaction Correction (TD-SIC) method, applying the Optimized Effective Potential (OEP) method. The new resulting scheme is called time-dependent “Generalized SIC-OEP”. A straightforward approximation, using the spatial localization of one set of orbitals, leads to the “Generalized SIC-Slater” formalism. We show that it represents a great improvement compared to the traditional SIC-Slater/KLI formalisms.

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Density Functional Theory (DFT) [1, 2] has become a standard theoretical tool for the description of electronic properties in a variety of physical and chemical systems, especially for sizable numbers of electrons. The extension of DFT to Time-Dependent (TD) situations [3] is a more recent achievement which also motivates numerous formal and practical investigations [4]. TDDFT constitutes to date one of the few, well founded theories, for describing dynamical scenarios in complex systems. From the point of view of applications TDDFT requires simple approximations, the simplest one being the Adiabatic Local Density Approximation (ALDA), which proved very useful in calculations of structure and low-amplitude excitations (optical response, direct one-photon processes) [1]. But self-interaction error plagues ALDA, which in particular spoils the dynamical description of excitations involving ionization, especially when close to threshold. A correct treatment requires a self-interaction correction (SIC), such the one proposed in [3]. This SIC has been used since then at various levels of refinement for structure calculations in atomic, molecular, cluster and solid state physics, see e.g. [6, 7, 8, 9]. But the SIC scheme leads to an orbital dependent mean field, which causes several formal and technical difficulties [10], becoming all the more cumbersome in the TD case. Applications of SIC in TD situations are thus mostly done in approximate manner, linearized [11], using averaged-density SIC [12], or relying on various approximations of TD Optimized Effective Potential (TDOEP) scheme [13] (the latter allows to deal with a common local potential). The most popular approximate OEP scheme is the Krieger-Li-Iafrate (KLI) approach [14, 15, 16] and, in a further step of simplification, the Slater approximation [17]. But both suffer from inconsistencies, such as violation of zero force theorem and energy conservation [18], even if some applications may be more forgiving [19].

We have recently generalized the considerations of stationary SIC [4] to the time dependent case [20] and showed that the time propagation of the “exact” SIC scheme can be performed thanks to a double basis set formulation (both sets being connected by a unitary transformation building the same total density). The resulting scheme satisfies all key formal properties. But the remaining potential becomes non-local, which substantially slows down numerical calculations. In the stationary case, a SIC-OEP scheme relying on this two sets technique can be performed leading to “Generalized SIC-OEP” either in full formulation [21] or in the “Generalized SIC-Slater” (GSlat) approximation [22] which emerges naturally because of the localization of one set of orbitals [22]. GSlat is numerically efficient and represents a great formal and practical improvement over traditional stationary SIC-Slater/KLI [22, 23]. It remains to extend Generalized SIC-OEP to the time domain and consider simple efficient approximations thereof, such as possibly the time-dependent GSlat (TDGSlat). It is the aim of this paper to address both aspects.

The starting point is the SIC energy functional for electrons (all sums run over occupied states only; we omit the dependencies when it is not misleading and we note $\rho = \sum_{\alpha} |\psi_{\alpha}|^{2}$)

$$E_{\text{SIC}} = \sum_{\alpha} (\psi_{\alpha} | \frac{p^{2}}{2m} | \psi_{\alpha}) + E_{\text{ext}}[\rho] + E_{\text{ALDA}}[\rho] - \sum_{\alpha} E_{\text{ALDA}}[|\psi_{\alpha}|^{2}]$$

The first term is the non-interacting kinetic energy, $E_{\text{ext}}[\rho] = \int d\rho v_{\text{ext}}$ where $v_{\text{ext}}$ stands for the interaction with the ionic background and any other local possibly time-dependent external field, and $E_{\text{ALDA}}[\rho]$ is a standard ALDA energy-density functional The last term corresponds to the SIC. We mention in passing that the SIC, and with it all our following development, does also apply to more general functionals as, e.g., the Generalized Gradient Approximation (GGA) [24]. The TDSC equations result from a variational principle applied to the action integral (here we use the standard action functional. Its causality and boundary conditions problems are discussed in [25, 26]). Furthermore, we explicitly include the orthonormality constraint with Lagrange multipliers.
This yields
\[ \delta \left( \text{ASIC} - \int_{-\infty}^{t_1} dt \sum_{\beta, \gamma} (\psi_\beta | \psi_\gamma) \lambda_{\gamma \beta} \right) = 0 \] ,
\[ \text{ASIC} = \int_{-\infty}^{t_1} dt \left( E_{\text{SIC}} - \sum_\alpha (\psi_\alpha | i \hbar \partial_t | \psi_\alpha) \right) \] . \tag{2}
leading to one-body equations that we recast as
\[ i \hbar \partial_t | \psi_\alpha \rangle = \hat{h}_{\text{SIC}} | \psi_\alpha \rangle \] \tag{3}
\[ \forall t : 0 = (\psi_\beta | U_{\text{ALDA}} \left| \psi_\alpha \right| \psi_\alpha) \] \tag{4}
where \( U_{\text{ALDA}} [\rho_\alpha] = (\delta E_{\text{ALDA}} [\hat{\rho}] / \delta \hat{\rho})_{\hat{\rho} = \rho_\alpha} \) and
\[ \hat{h}_{\text{SIC}} = \hat{h}_{\text{ALDA}} - \sum_\alpha U_{\text{ALDA}} \left[ | \psi_\alpha \rangle \right] \left( \psi_\alpha \right) (5) \]
\[ \hat{h}_{\text{ALDA}} = \frac{p^2}{2m} + v_{\text{ext}} + U_{\text{ALDA}} [\rho] . \]

Note that \( \hat{h}_{\text{SIC}} \) is applied to the \emph{diagonal orbitals} \(| \varphi_\alpha \rangle \) in Eq. (3), but is calculated with the \emph{localized orbitals} \(| \psi_\alpha \rangle \) in Eq. (4). The \(| \varphi_\alpha \rangle \)'s are related to the \(| \psi_\alpha \rangle \)'s by a unitary transformation
\[ \psi_\alpha = \sum_i \varphi_i u_{i\alpha} ; \sum_i u_{i\alpha} \varphi_{i\beta} = \delta_{\alpha \beta} . \tag{6} \]
The wave functions \( \varphi_i \) and the transformation coefficients \( u_{i\alpha} \) are varied independently where variation with respect to \( \varphi_i \) yields Eq. (5) and variation of the \( u_{i\alpha} \) then leads to the symmetry condition (3) [20, 27]. The symmetry condition guarantees conservation of orthonormality and enforces localization of the states \(| \psi_\alpha \rangle \) [27]. It thus plays a key role in this formalism. Although Eq. (3) has proven to be tractable numerically [20, 27], the corresponding Hamiltonian is non-local, see Eq. (5), which implies a very high numerical cost.

To develop a simplified scheme while maintaining locality, we apply this double set formulation to the TDOEP scheme. We start from the action integral (2). The previous considerations on the \textquotedblleft exact\textquotedblright SIC energy showed that it should be expressed with the localized \( \psi_\alpha \), which satisfy the symmetry condition (4). We stationarize the action, imposing that the diagonal \( \varphi_i \) (linked by a unitary transformation to the \( \psi_\alpha \)) satisfy a Kohn-Sham like equation with a local and state-independent potential \( V_0 \) (although OEP orbitals are not exactly the same as the SIC ones, we employ the same notations to keep the presentation compact)
\[ [\hat{h}_{\text{ALDA}} - V_0 (r, t)] \varphi_i (r, t) = i \hbar \partial_t \varphi_i (r, t) . \tag{7} \]
The orthonormality constraint is implicitly contained in (4). The result will thus be considered as a local approximation of the SIC Hamiltonian [43]. The optimized effective potential \( V_0 (r) \) is found by the variation \( \delta A_{\text{SIC}} / \delta V_0 (r, t) \) which employs variations with respect to the \( \varphi_i \) through the chain rule for functional derivatives. The independent variation of the coefficients \( u_{i\alpha} \) in the transformation (4) remains as before. We obtain
\[ \sum_i \int_{-\infty}^{t_1} dt' \intdr' \left( V_0 (r', t') - v_i^* (r', t') \right) \]
\[ \times K_i (r, t; r', t') \varphi_i^* (r', t') \varphi_i (r, t) + \text{c.c.} = 0 \] \tag{8}
\[ V_i (r, t) = \frac{1}{\varphi_i (r, t)} \delta \varphi_i^* (r, t) \int_{-\infty}^{t_1} dt' \sum_\alpha E_{\text{ALDA}} [\psi_\alpha] (r', t') \]
\[ = \frac{1}{\varphi_i (r, t)} \sum \psi^*_\alpha (t) U_{\text{ALDA}} [\psi_\alpha] \left( \psi_\alpha \psi_\alpha \right) (r, t) . \tag{10} \]
to be fulfilled together with the symmetry condition (4) which again results from variation of the \( u_{i\alpha} \). This is the TD \textquotedblleft Generalized SIC-OEP\textquotedblright formalism. The new feature in this double-set TDOEP appears in the \( v_i \) which now employs the localized \( \psi_\alpha \), in accordance with exact TDSIC. The previous applications of TDOEP to SIC as found in [10] used the action (4) written in terms of the diagonal \( \varphi_i \), which leads to well known pathologies, as the incapability of the traditional SIC-Slater/KLI approximations to reproduce the spatial localization. Eq. (8) can be rewritten equivalently as
\[ V_0 = \Re \{ V_S + V_K + V_C \} - \Im \{ V_{\text{TD1}} + V_{\text{TD2}} \} \]
where \( V_S, V_K, V_C \) are defined as
\[ V_S = \sum_i | \varphi_i |^2 / \rho v_i , \tag{11} \]
\[ V_K = \sum_i | \varphi_i |^2 (\varphi_i | V_0 - v_i | \varphi_i) , \tag{12} \]
\[ V_C = \frac{1}{2} \sum_i \nabla_i (\rho \nabla_i | \varphi_i |^2) / \rho , \tag{13} \]
\[ p_i (r, t) = \frac{1}{\varphi_i^* (r, t)} \int_{-\infty}^{t_1} dt' \int dr' \left( V_0 (r', t') - v_i^* (r', t') \right) \]
\[ \times \varphi_i^* (r', t') K_i (r, t; r', t') . \tag{14} \]
To those potentials, which also appear in the stationary case, one has to add purely time-dependent contributions
\[ V_{\text{TD1}} = \frac{1}{\rho} \sum_i \frac{\nabla^2 | \varphi_i |^2}{4} \int_{-\infty}^{t} dt' (\varphi_i (t') | v_i (t') | \varphi_i (t')) \]
\[ V_{\text{TD2}} = \frac{1}{\rho} \sum_i (| \varphi_i |^2 \partial p_i / \partial t + J_i \cdot \nabla p_i) \] \tag{15}
where \( J_i = \frac{\hbar}{2im} (\varphi_i \nabla \varphi_i - \varphi_i \nabla \varphi_i^* ) \) is the current density. Some straightforward manipulation with the uni-
The "Generalized SIC-KLI" approximation $V_K$ has not the form that might be intuitively expected \[21\]. Moreover, as $(\phi_i|\psi_i) = (\phi_i|\psi_i)$, we have, with \[13\], $3m \{V_{TD1}\} = 0$.

It turns out that the full TD "Generalized SIC-OEP" scheme is very costly numerically, even more than the "exact" TDSIC formalism because time integrals (memory effects) appear explicitly in the definition of $V_0$. Thus we propose a strong simplification which emerges naturally from the fact that the $\psi_\alpha$ remain spatially very localized \[21\]. This means that, at all time, at a given $r$, one single $\psi_\alpha$, mostly dominates the other wave functions $\psi_\beta \neq \alpha$ and thus

$$\sum_\beta \frac{|\psi_\beta|^2}{\rho} U_{ALDA}[|\psi_\beta|^2] \psi_\alpha \approx U_{ALDA}[|\psi_\alpha|^2] \psi_\alpha. \quad (17)$$

One finds that the Slater contribution $V_S$ is dominating, although the other terms are generally non negligible. But in the TD "Generalized SIC-OEP", if we approximate $V_0 \approx V_S \approx \sum_\alpha \frac{|\psi_\alpha|^2}{\rho} U_{ALDA}[|\psi_\alpha|^2]$, the localization (i.e. Eq. (17)) amounts to have almost vanishing $V_K$ and $p_r$, see Eq. (16), and thus almost vanishing $V_C$ and $V_{TD2}$, see Eqs. (13) and (15). Thus, the TDOEP result naturally reduces to

$$V_0 \approx \sum_\alpha \frac{|\psi_\alpha|^2}{\rho} U_{ALDA}[|\psi_\alpha|^2] \quad . \quad (18)$$

Eq. (4) generates the set $\phi_i$ of diagonal states, which can be interpreted (to first order) as single electron orbitals, while the unitary transformation (4) serves to accommodate the symmetry condition (4), which, in turn, defines the localized orbitals $\psi_\alpha$ entering the potential $V_0$ as given in Eq. (13). Note that this equation has the form of a Slater approximation [28] but is constructed from the localized $\psi_\alpha$ and applied to the $\phi_i$. This is the time-dependent extension of the "Generalized SIC-Slater" scheme (TDGSlat). We showed in [22] that its stationary counterpart solves many problems encountered with traditional SIC-Slater/KLI methods.

We first check the performance of TDGSlat as compared to full TDSIC in Fig. 4. Times are shown relative to the time needed to propagate the cheapest solution (ALDA) for Hydrogen chains on a given physical time interval (mind the logarithmic scale). The gain as compared to TDSIC is dramatic (typically of an order of magnitude) for a cost an order of magnitude larger than ALDA, for $H_8$.

It is well known that standard (one set) SIC-Slater and KLI approximations suffer from inconsistencies in the time domain. They can strongly violate energy conservation and zero force theorem (ZFT) [18], while neither full TDSIC [27] nor full "Generalized SIC-OEP" do suffer from these defects, but at the price of very heavy numerical cost. Strictly speaking, at TDGSlat level one has (for a non-explicitly TD external potential)

$$\partial_t E_{SIC} = \frac{\hbar}{m} \sum_\alpha 3m \int dr$$

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initial (ground state) electronic distributions which simulta-
eously both examples we plot the time evolution of the total
full 3D using the same numerical methods as in [27]. In a small metallic cluster. Calculations have been done in quantum dot with 6 electrons, in the spirit of [29], and our results in Figures 2 and 3 on two typical cases: a

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which in principle leads to energy and ZFT violation as well. However, the localization of the $\psi_\alpha$, which implies the approximate relation [17], lets us hope that TDGSlat produces “less” violated energy conservation and zero-

force theorem, where “less” means that the conservation laws remain stable for a longer time span than in simple SIC-Slater/KLI. This alone could be progress for many practical purposes. It is thus a key issue to explore how TDGSlat practically performs in the time domain. This has been done in a variety of systems and we illustrate our results in Figures 2 and 3 on two typical cases: a quantum dot with 6 electrons, in the spirit of [28], and a small metallic cluster. Calculations have been done in full 3D using the same numerical methods as in [27]. In both examples we plot the time evolution of the total energy and the dipole moment after a small boost of the initial (ground state) electronic distributions which sim-

ulates a very short laser pulse, and still allows to check energy conservation in time because the excitation field is switched off during propagation. We take care of consid-

ering sufficiently moderate perturbations to remain in the linear domain (excitation energy a few percent of the typ-

cal electronic level spacing) and we follow the dynamics over "long" times, typically over 100 eigenperiods of the system, as seen from the dipole oscillations. We restrict the calculations to TDGSlat and SIC-Slater. Full SIC calculations on such long times are prohibitively costly. We have checked on shorter times that they deliver per-

fect energy and ZFT conservation.

Both figures deliver the same message and we thus dis-


cuss them together. While both full SIC and TDGSlat dynamics remain remarkably stable in time, standard SIC-Slater exhibits a sizeable violation of energy and ZFT (seen through the unstability of the dipolar momen-
t [18]). In the case of energy one observes a strong drift in time while for the dipole moment oscillations become extremely large (much larger than the original ones). When pursuing the TDGSlat over even longer times one observes a small energy violation, as expected on formal grounds. Still the effect is rather small and much delayed as compared to standard SIC-Slater. And the most important point is that the drift occurs on sufficiently long times so that relevant physics can be studied for shorter times. One can thus conclude that dynamics in the linear domain is controlled in TDGSlat, remaining very close to full TDSIC over long times.

To summarize, we started from the two basis set formulation of TDSIC and applied the TDOEP formalism to recover locality, resulting to the time-dependent “Generalized SIC-OEP” formalism. As it is very costly numerically, we looked for a much less costly relevant approximation, which naturally comes from the localized character of the $\psi_\alpha$ set and is called time-dependent “Generalized SIC-Slater”. By virtue of the double-set technique, it has a wider range of applicability than tradi-
tional SIC-Slater/KLI approximations. In particular, we checked formally and numerically on various systems (organic, metal, quantum dot) that TDGSlat will satisfy much better energy and ZFT conservation.

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