

# The Self Interaction Correction Revisited

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**Abstract.** We provide a brief outline of the Self Interaction Problem in the Local Density Approximation of Density Functional Theory. We discuss how the problem can be circumvented by a clean formulation of the theory and show a few examples of applications of a newly introduced simplified formulation of the theory.

## 1 Introduction

The study of the dynamics of finite systems under strong perturbations has focused numerous investigations in the past in many domains of science (nuclear collisions [1], plasma physics [2], electronic dynamics [3, 4]). From the theoretical point of view, the problem still raises several difficulties and thus calls for the formulation of well founded theories. The goal of our investigations is to study explicitly the dynamics of clusters and molecules subject to an irradiation by a laser or a charged projectile. We furthermore require a high degree of accuracy at low energy in order, in particular, to be able to analyze phenomena close to ionization threshold. With such constraints, Density Functional Theory (DFT) [5, 6], extended in the time domain (Time Dependent DFT, TDDFT) [7] appears as the most promising theory for addressing such questions. Density Functional Theory has provided a major tool of investigation for numerous physical and chemical systems over the last few decades, both for static and dynamical problems. It thus now constitutes a well founded theoretical basis on which to develop accurate approaches. It nevertheless still raises numerous formal difficulties and we shall discuss here one the well known pathology, namely the Self Interaction Correction (SIC) problem.

The simplest approximation to DFT is the well known Local Density Approximation (LDA) which provides a simple ansatz for the account of exchange and correlation effects on the basis of a Fermi Gas approximation. The LDA approximation provides an extremely useful tool in DFT because of its simplicity and robustness. It furthermore constitutes a sound basis for many theoretical developments. It nevertheless suffers from a self interaction problem, that is the fact that when one electron interacts with the mean-field, which is a functional of the total density (hence including the electron itself), this implies that it also interacts with itself. This is a priori a generic pathology of mean-field, but it is explicitly cured by the exchange term, for example in the Hartree-Fock approximation. The approximate LDA exchange does not suffice to make such a cancellation properly, which leads to a spurious residual

self interaction. This defect can have sizable consequences on the physical description of the systems we are interested in. We thus have to correct for this defect by dedicated theories. This is the aim of this contribution to discuss such strategies.

The paper is organized as follows. After a brief introduction on electronic systems, we switch to DFT and LDA and illustrate the SIC problem on a typical example. We then introduce standard SIC approaches and 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 a typical example. We finally conclude and discuss a few perspectives on dynamical applications.

## 2 About Electronic Systems

In this section, we shall certainly not cover all aspects associated to electronic systems. We rather aim at providing a few key ideas concerning some of their basic properties in complex systems and which differ from the case of nuclear systems. In a second step, we briefly recall a few observables considered for describing electronic systems, in particular in relation to irradiation processes. Any finite electronic system involves a background of ions to which electrons are associated to form a molecule or a cluster. Ions can in most cases be treated as classical particles and since they are very massive as compared to electrons, there is no basic problem with the definition of the center of mass in such systems, at variance with the nuclear case.

Another aspect which deserves some discussion concerns the impact of exchange in electronic systems. In a neutral molecule or cluster, binding dominantly comes from Coulomb exchange (typically about 3/4). This is illustrated in Figure 1 in which are plotted the various contributions to the electronic mean-field in the case of  $\text{Na}_{138}$  with soft jellium (original jellium approach complemented by an effective treatment of surface by softening). The upper panel shows that jellium and electron densities stay indeed very close to each other (up to quantum oscillations of the electronic density), which minimizes the direct Coulomb energy. The lower panel of Figure 1 shows the effective electronic potential and its separate contributions. The (extremely small) part labelled “direct Coulomb” is the total Coulomb field from electrons and jellium background. Even with a detailed account of ions, it would remain small. The largest contribution to cluster binding comes from the exchange energy and, to a lesser extent, from the correlation energy (20–30%).

To end this section, we schematically sort observables of electronic systems, both finite and bulk, in three main classes (with soft porous boundaries though): intrinsic single particle properties, global structure ones and properties in direct relation to the response to electromagnetic fields. Among single particle properties, let us especially mention the density of states and band gap in solids. The work function in solids corresponds to the Ionization Potential (IP) in finite systems and is known as separation energy in nuclei. All these single particle properties have been well studied in a variety of systems both experimentally and theoretically. Bond

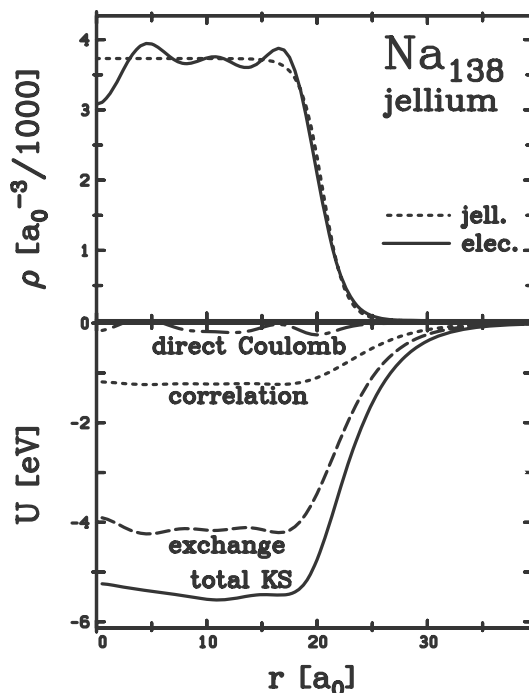


Figure 1. Electronic and ionic densities (upper panel) and effective electronic field (Kohn-Sham potential, see section 3) for  $\text{Na}_{138}$  computed with the energy functional of [8] and soft jellium background ( $r_s = 3.93 a_0$ , width  $\sigma = 1 a_0$ ). From [4].

lengths and dissociation energies in molecules or clusters lie among global structure properties. They can be read off from computed potential energy surfaces and are usually measured very accurately. Potential energy barriers between isomers or reaction channels are usually more difficult to access but data exist as well. Finally the response to electromagnetic fields involves several key quantities such as, in particular, the static and dynamical polarizability of a finite system, and also magnetic moments. Other key quantities, such as IP and dissociation energies, although often considered as static quantities, actually play a key role in the understanding of irradiation processes we aim at describing. We shall thus focus a sizable part of our discussions on these quantities, using them as illustrative examples.

### 3 From DFT to LDA

There exist a bunch of well documented presentation of DFT, LDA and TDDFT and we refer the reader to these various references for more details [5–7]. We just briefly introduce the key ingredients necessary for the further discussions. We only discuss electrons here, ions being treated as classical particles all over. We work in

the so-called Kohn-Sham [9] scheme of DFT in which the system is represented by a set  $\{\psi_\alpha, \alpha = 1, \dots\}$  of single electron wavefunctions. The latter serve to construct the one-body density,  $\rho = \sum_\alpha |\psi_\alpha|^2 = \sum_\alpha \rho_\alpha$ , key ingredient of DFT according to Hohenberg and Kohn's theorem [10]. The resulting theory resembles an effective mean-field theory involving a single electron Hamiltonian,  $h[\rho] = h_0 + U_H + U_{xc}$ , where  $h_0 = -\frac{\hbar^2}{2m}\Delta$  is the kinetic term,  $U_H$  the Hartree (direct) Coulomb interaction, and the exchange correlation term which is a functional of the density  $\rho(\mathbf{r})$  and which has to be properly chosen.

The simplest approximation for  $U_{xc}$  is provided by the Local Density Approximation (LDA). It consists in calculating this term assuming that the system is infinite and homogeneous and take this value locally. This amounts to make the replacement  $U_{xc}[\rho^\infty] \rightarrow U_{xc}[\rho(\mathbf{r})]$  where  $\rho(\mathbf{r})$  is the local density and  $\rho$  the density of the corresponding infinite system with homogeneous density  $\rho(\mathbf{r})$ . The exchange correlation term thus becomes a simple function of the local density  $\rho(\mathbf{r})$  and in the following we denote by  $U_{\text{LDA}}$  the corresponding one-body potential ( $U_{\text{LDA}} = U_H + U_{xc}$ ). By construction, LDA should be valid only for systems in which the density  $\rho(\mathbf{r})$  varies sufficiently slowly. In fact, it performs much better than expected and can be successfully applied to situations with nonvanishing density gradients. Note that cancellation errors occur in the exchange correlation terms, so that they usually perform globally better when plugged together in a LDA functional rather than when optimizing separately exchange and correlation terms. Generally speaking, LDA performs well for the computation of total energies, from which for example one can extract ionization potentials by differences. Dissociation energies are usually attained within 10–20% as well. One should furthermore note that LDA exhibits good formal features, at variance with some other DFT methods (see section 5). The LDA is thus a tremendously good approximation in view of its simplicity. And as stated by Kohn [6], it is so to say the mother of most approximations in DFT. It is thus interesting to see how it performs in a few typical systems.

We start with an example from solid state physics. Lattice constants of a few systems, from simple covalent ones as C, Si, Ge, to mixed ones as AlN, SiC, GaN, AlAs and GaAs, have for example been computed in LDA and compared to experimental values. In all the cases the error to experiments is remarkably small,  $\sim 1\text{--}2\%$ . The next example concerns the optical response in a simple metal cluster, presented in Figure 2. We compare semi-classical and TDLDA results with experimental data [11] together with results from ab initio Configuration Interaction quantum chemistry calculations [12]. All calculations compare reasonably well to experiments, even LDA in the semi-classical approximation. We finally consider the example of simple dimer molecules in which key quantities are the bond length  $r_e$  (equilibrium distance between the two atoms), the dissociation energy  $D_e$  (energy required to break the ground state dimer into two isolated atoms) and vibration frequency at equilibrium  $\omega_e$ . We take a set of LDA results from standard LDA calculations [13] applied to 13 typical molecules ( $\text{H}_2, \text{Li}_2, \text{B}_2, \text{C}_2, \text{O}_2, \text{N}_2, \text{F}_2, \text{Na}_2, \text{Al}_2, \text{Si}_2, \text{P}_2, \text{S}_2, \text{Cl}_2$ ) including covalent and metallic bonds. As compared to experimental values, the average over LDA results leads to an agreement of order 1% for

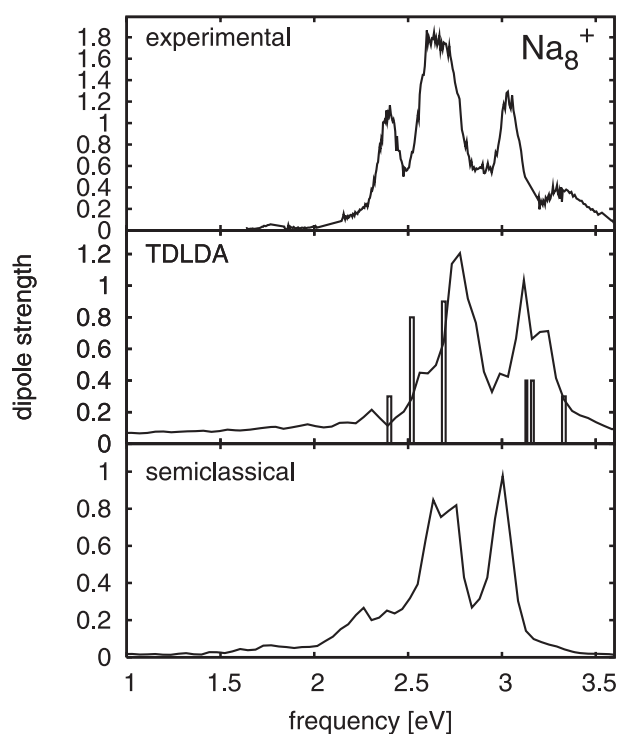


Figure 2. Optical absorption strengths for the cluster  $\text{Na}_8^+$  with experimental spectra (top) [11], quantum (middle) and semi-classical results (bottom) displayed as indicated. The strengths from configuration interaction calculations [12] are indicated as bars in the middle panel.

$r_e$ , about 24 % for  $D_e$  and 3% for  $\omega_e$ , which is altogether quite encouraging. LDA thus provides a very sound starting basis for DFT calculations in many domains of physics and chemistry.

#### 4 The SIC Problem

In spite of its many successes, LDA suffers the self interaction problem since the approximate exchange term does not cancel exactly the self interaction contribution in the direct term, as is for example the case in Hartree Fock calculations. As a side remark, note that this problem does not appear crucial in nuclear systems because of the short range of the nuclear interaction. Indeed, when using an effective zero range interaction, it can even be exactly solved. There only remains the correction to the Coulomb term but, even in proton-rich nuclei, it does not seem that an approximate treatment of Coulomb exchange might have an experimentally visible impact. The situation is completely different in electronic systems in which, as al-

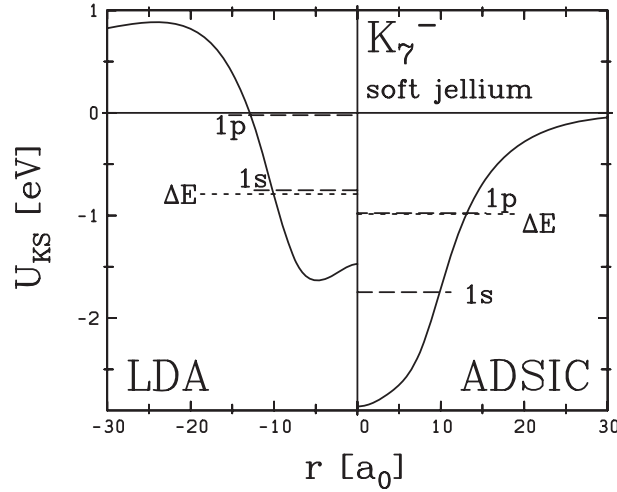


Figure 3. Comparison between LDA and ADSIC for  $K_7^-$  with soft jellium background ( $r_s = 5.0 a_0$ ,  $\sigma_{jel} = 1.37 a_0$ ). Compared are: the net Kohn-Sham potentials (full lines), the single electron energies (dashed lines), and the one-electron separation energy  $\Delta E = E(K_7^-) - E(K_7)$  (dotted lines). The left panel shows results from LDA and the right panel from ADSIC (see section 5). From [4]

ready mentioned, (Coulomb) exchange provides about 3/4 of the total binding of a system. And, in that case, the poor treatment of the self interaction leads to measurable pathologies. The simplest example is provided by the IP which sensitively depends on the self interaction. Indeed LDA 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) which leads to an incorrect IP. The effect is especially strong when the IP is small, as in the case of anionic clusters. Figure 3 shows the example of  $K_7^-$  and demonstrates the typical pathology in the evaluation of IP: LDA violates Koopmanns' theorem as the IP, evaluated from the energy difference  $\Delta E$ , strongly differs from the energy of the least bound state (here a 1p level). Moreover the energy of the 1p level is vanishingly small, which is wrong. Finally the electronic potential exhibits an unphysical bump at intermediate distances. All in all, LDA badly fails in that case and calls for a correction of the self interaction (SIC) problem.

## 5 Self Interaction Correction and Optimized Effective Potential

The basic SIC method consists in subtracting “by hand” the spurious self interaction [14, 15]. As compared to the LDA energy, this amounts to define a SIC energy  $E_{SIC}$  and the corresponding one-body Hamiltonian, obtained from variation of  $E_{SIC}$  with respect to  $\psi_\alpha^*$ , as follows:

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

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

where  $U_{\text{SIC},\alpha} = U_{\text{LDA}}[\rho] - U_{\text{LDA}}[\rho_{\alpha}]$ . The key point here is that the resulting one-body Hamiltonian does depend on the orbital on which it acts, which has disastrous consequences. This a priori breaks the orthonormality of the  $\psi_{\alpha}$  and should thus severely plague any time dependent SIC calculations, if formulated that way. The problem is well known since the early days of SIC methods. A way out would be to be able to construct a (even if approximate) single one-body Hamiltonian common to all orbitals.

There fortunately exists a general method to do so, applicable on any mean-field theory (such as Hartree Fock in particular) and which is known as the Optimized Effective Potential (OEP) [16, 17], actually introduced much earlier than SIC. The idea beyond is remarkably simple and elegant. It first consists in parametrizing by the common (optimal) potential  $V_0$  the single particle orbitals  $\varphi_i^{V_0}$ . We have introduced on purpose a new notation in order to properly distinguish these orbitals from the original  $\psi_{\alpha}$  wavefunctions which a priori act in a larger Hilbert space. We then write down the total energy (Hartree-Fock, SIC, ...) with these parametrized wavefunctions. We finally optimize this energy with respect to the potential  $V_0$ . This provides as a first step  $V_0$ , then the associated wavefunctions  $\varphi_i^{V_0}$ , and finally amount to solve the problem in a restricted space. Applied to our SIC problem, one can thus formally summarize the SIC-OEP procedure by :

$$h_{\text{OEP}} |\varphi_i^{V_0}\rangle = (h_0 + V_0) |\varphi_i^{V_0}\rangle = \varepsilon_i |\varphi_i^{V_0}\rangle, \quad (3)$$

$$E_{\text{OEP}} = E_{\text{SIC}}[\{\varphi_i^{V_0}\}], \quad (4)$$

$$\frac{\delta E_{\text{OEP}}}{\delta V_0} = 0 \rightarrow V_0 \rightarrow \varphi_i^{V_0}. \quad (5)$$

Once optimization is performed,  $V_0$  can be separated in 3 components (corresponding to various degrees of approximations),  $V_0 = V_S + V_K + V_C$ , in which  $V_S$  is the simplest Slater approximation [18],  $V_K$  the complementing term leading to the well known KLI approximation ( $V_S + V_K$ ) [19] and  $V_C$  is a correction usually assumed small. Explicit expressions for these various terms can be derived, but most calculations have been performed at Slater or KLI levels, the full OEP-SIC equations being in most cases impossible to solve in practical cases. For a further comparison, let us write down the Slater term :

$$V_S = \sum_i \frac{|\varphi_i^{V_0}|^2}{\rho} U_{\text{LDA},i}, \quad (6)$$

where  $U_{\text{LDA},i} = U_{\text{LDA}}[|\varphi_i^{V_0}|^2] = U_{\text{LDA}}[\rho_i]$ . Note that the Slater approximation can be further simplified to provide the so-called Average Density SIC (ADSIC) [20] by replacing  $\rho_i$  by  $\rho/N$  where  $N$  is the total number of electrons in the system. This

particularly simple ADSIC approximation has been recently proposed and successfully applied to metal clusters [20] and polyacetylene chains [21]. An example of its performance is given in the right panel of Figure 3 where one can see that it remarkably solves the IP problem discussed at that place: Koopmann's theorem is restored and the theoretical energy of the 1p level comes fairly close to the experimental separation energy.

Nevertheless, neither ADSIC nor the more involved Slater or KLI approximations are fully satisfying. One can easily show that Slater and KLI for example violate key formal properties, especially when extended to the time domain (energy conservation and zero force theorem). Even in the static domain, the situation is not fully satisfying, by far. An example is given in Figure 4 in which the ground state potential energy surface of the simple Carbon dimer is presented in various DFT approaches. The LDA (LSDA in that case because spin has been properly taken into account) presents an acceptable qualitative behavior, but it misses the ground state energy and strongly misses the vibration frequency. All SIC calculations perfectly reproduce ground state (bond length, ground state energy, vibration frequency), which is a welcome feature. But, they badly miss the shape of the potential energy surface at intermediate distances. This is a known pathology of such theories linked to localization problems at the side of single electron wavefunctions. This raises a severe problem as it in particular makes dissociation properties hardly acceptable, a key issue when considering irradiation processes. These defects call for an improvement of SIC approaches, both in its full and OEP approximated versions. This is what is discussed in the following section.

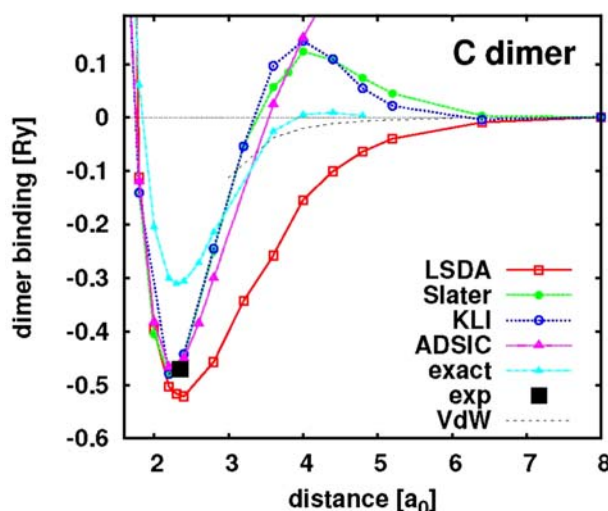


Figure 4. Potential energy surface of the dimer  $C_2$  calculated with various DFT schemes, with or without SIC. The full square indicates the experimental values of the bond length and the binding energy.



## 6 SIC Revisited

The basic primary defect of the original SIC formulation is the fact that it does not ensure a proper orthonormalization of single electron orbitals, as the variational principle applied to the SIC energy delivers orbital dependent fields. A simple way out of this problem is to enforce orthonormalization of the wavefunctions inside the variational principle by means of a set of Lagrange parameters  $\lambda_{\beta\alpha}$ . For then, the variational principle reads

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

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 enforced orthonormality leads to the second equation called “symmetry condition” which becomes a crucial ingredient of the theory. Because the formulation is variational, there necessarily exists a solution to this set of equations in spite of its apparently very involved form. The enforcement of orthonormalization in SIC calculations was proposed sometimes ago in static calculations [22, 23] but the formalism was only very recently extended in the time domain [24]. The case of time dependent processes is much more cumbersome than the static case, at least from a practical point of view and we shall thus not further elaborate on it here. Still it is interesting to note that the time dependent case has led to introduce two sets of single electron orbitals to lead to a practical solution of the problem and this double set strategy turns out to be extremely useful also in the static case.

The idea behind the double set strategy is to exploit a degree of freedom which is usually neglected in DFT, namely the principle possibility to perform unitary transforms among the single electron orbitals. In practice, we thus introduce two sets of single electron orbitals linked by an unitary transform. The first set  $\{\psi_\alpha\}$ , as naturally introduced above, serves to fulfill the symmetry condition Eq. (9). It turns out that it provides usually well localized wavefunctions. The second set  $\{\varphi_i\}$  serves to diagonalize the SIC Hamiltonian, Eq. (8), and corresponds more to “physical” wavefunctions to the extent that one can for then associate one single electron energy to each wavefunction. Both sets have thus their advantages and can be very different. As such, the interest of the double set strategy is nevertheless rather limited in a static full SIC approach. But it becomes very interesting when considering SIC-OEP. One intuitively sees that the  $\{\varphi_i\}$  are probably structurally close to the SIC-OEP  $\varphi_i^{V_0}$  wavefunctions. Indeed, when properly formulated, the new SIC-OEP theory based on the double set strategy allows to derive a very accurate version of the Slater approximation, the Generalized Slater (GSlat) approximation [25]. Because of the localization of the  $\{\psi_\alpha\}$  wavefunctions, one can formally demonstrate

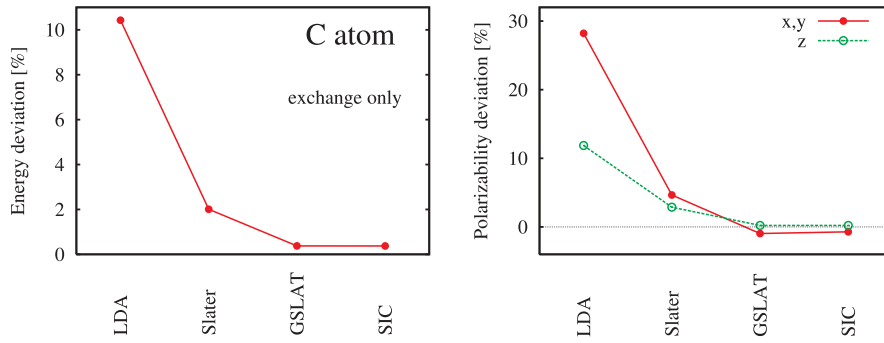


Figure 5. Comparison of various approaches for the C atom. Left panel: Deviation of binding energy from the Hartree-Fock benchmark value. Right panel: Deviation of dipole polarizabilities (in  $x$ ,  $y$ , and  $z$  directions) from the Hartree-Fock values [25].

that the usual Slater approximation becomes accurate, provided the potential is expressed in terms of the  $\{\psi_\alpha\}$ , while the OEP problem remains solved at the level of the  $\varphi_i^{V_0}$  wavefunctions. This formally reads

$$h_{\text{OEP}} |\varphi_i^{V_0}\rangle = \varepsilon_i |\varphi_i^{V_0}\rangle, \quad (10)$$

$$V_0 \simeq V_{\text{GSlat}} = \sum_\alpha \frac{|\psi_\alpha|^2}{\rho} U_{\text{LDA}}[|\psi_\alpha|^2], \quad (11)$$

with both sets connected by the proper unitary transform. This GSlat provides results extremely close to the full SIC ones. For example, it restores dissociation properties of  $\text{C}_2$ . Mind that full SIC has no problem for  $\text{C}_2$ ; these are the approximations to SIC-OEP which raise problems. The interest of this GSlat approximation is illustrated in Figure 5, where total energy and polarization of a carbon atom are displayed for various theories. To check the theory in a simple framework, we consider here an exchange only calculation for which Hartree Fock becomes the benchmark. Results are clear from Figure 5 with a remarkable accuracy attained by full SIC and an equally good quality by GSlat. More examples of observables have been considered and all lead to a similar conclusion.

## 7 Conclusions

We have discussed the SIC problem in finite electronic systems and proposed an improved scheme for solving several of the original pathologies of SIC. The self interaction problem is a well known defect of LDA in which exchange is treated in an approximate manner. Although LDA is able to reproduce many key data in electronic systems, it is unable for example to properly describe ionization properties because of this self interaction problem. The SIC method has been introduced to cure that problem. It nevertheless also suffers from pathologies linked to the fact that it does

not ensure orthonormalization of wavefunctions by construction. The OEP method can then be used in conjunction to SIC to derive a formally clean approximate theory to full SIC, at the price of producing extremely involved equations. The simplest approximations to these equations, the Slater and KLI approaches have been used in many occurrences but they still suffer from severe defects both formally and practically. We have thus proposed to revisit the SIC problem by reformulating the theory within explicitly enforcing orthonormalization. We have furthermore developed a two set strategy, which is practically compulsory in the time domain, but which also exhibits interesting properties in static problems. In particular, it allows to derive an extension of the Slater approximation, the Generalized Slater approximation which provides, at least for static problems, a remarkably accurate approximation to full SIC and allows to cure many pathologies of standard Slater and KLI calculations.

## Acknowledgements

The authors thank the French-German exchange programs PROCOPE, Institut Universitaire de France, Humboldt fundation and French ministry of research (Gay-Lussac award) for financial support during the realization of this work.

## References

1. G. F. Bertsch, A. Das Gupta, Phys. Rep. **160**, 190 (1988); Y. Abe, S. Ayik, P.-G. Reinhard, E. Suraud, Phys. Rep. **275**, 49 (1996).
2. S. Ichimaru, H. Iyetomi, S. Tanaka, Phys. Rep. **149**, 91 (1987).
3. F. Calvayrac, P.-G. Reinhard, E. Suraud, C. A. Ullrich, Phys. Rep. **337**, 493 (2000).
4. P.-G. Reinhard, E. Suraud, *Introduction to Cluster Dynamics*, (Wiley, New York, 2003).
5. R. M. Dreizler, E. K. U. Gross, *Density Functional Theory: An Approach to the Quantum Many-Body Problem*, Springer-Verlag, Berlin, 1990.
6. W. Kohn, Rev. Mod. Phys. **71**, 1253 (1999).
7. M. A. Marques, C. A. Ullrich, F. Nogueira, A. Rubio, K. Burke, E. K. Gross, *Time Dependent Density Functional Theory*, Lect. Notes in Physics, **706**, Springer, Berlin, 2006.
8. J. P. Perdew, Y. Wang, Phys. Rev. B **45**, 13244 (1992).
9. W. kohn, L. J. Sham, Phys. Rev. **140**, 1133 (1965).
10. P. Hohenberg, W. kohn, Phys. Rev. **136**, 864 (1964).
11. H. Haberland, M. I. Schmidt, Eur. Phys. J. D **6**, 109 (1999).
12. V. Bonacic-Koutecky, J. Pittner, C. Fuchs, P. Fantucci, M. F. Guest, J. Koutecky, J. Chem. Phys. **104**, 1427 (1996).
13. R G Parr, W Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
14. J.P. Perdew, Chem. Phys. Lett. **64**, 127 (1979).
15. S. Kümmel, L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).
16. R. T. Sharp, G. K. Horton, Phys. Rev. **90**, 317 (1953).
17. J. D. Talman, W. F. Shadwick, Phys. Rev. A **14**, 36 (1976).
18. J. C. Slater, Phys. Rev. **81**, 385 (1951).

19. J. B. Krieger, Y. Li, G. J. Iafrate, *Phys. Lett. A* **146**, 256 (1990).
20. C. Legrand, E. Suraud, P.-G. Reinhard, *J. Phys. B* **35**, 1115 (2002).
21. I. Ciofini, C. Adamo, H. Chermette, *J. Phys. Chem.* **123**, 121102 (2005).
22. M. Pederson, R. A. Heaton, C. C. Lin, *J. Chem. Phys.* **80**, 1972 (1984).
23. S. Goedecker, C.J. Umrigar, *Phys. Rev. A* **55**, 1765 (1997).
24. J. Messud, P. M. Dinh, P.-G. Reinhard, E. Suraud, *Phys. Rev. Lett.* **101**, 096404 (2008).
25. J. Messud, P. M. Dinh, P.-G. Reinhard, E. Suraud, *Chem. Phys. Lett.* **461**, 316 (2008).