

5 SCIENTIFIC HIGHLIGHT OF THE MONTH

Self-Interaction Correction in Density Functional Theory: The Road Less Traveled

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Two roads diverged in a yellow wood,
And sorry I could not travel both
And be one traveler, long I stood
And looked down one as far as I could
To where it bent in the undergrowth . . .
Robert Frost, *The Road Not Taken*, 1920

Abstract

The 30th anniversary of the Perdew-Zunger paper on the self-interaction correction (SIC) of density functional approximations to the exchange-correlation energy was marked by a recent conference that focused on the theoretical and computational formalism and on diverse applications to insulators, strongly-correlated materials, charge transfer, transport, optical properties, magnetism and excited states. Here we present some highlights from *Self-Interaction Correction: State of the Art and New Directions*.

1 Introduction and background

The thirtieth anniversary of the Perdew-Zunger paper [1] on the self-interaction correction to density functional approximations was the occasion for a celebratory conference, “Self-Interaction Correction: State of the Art and New Directions”, held 19-21 September 2011 in Chester, England. The conference was organized by Zdzislawa Szotek, Leon Petit, and Martin Lueders of STFC Daresbury Laboratory and sponsored by the European Science Foundation, the Daresbury node of CECAM (directed by Walter Temmerman), and Psi-k. It ended with a round-table discussion moderated by Malcolm Stocks. This highlight will present some impressions of the subject and the conference. We attempt to provide a discussion on all subject matter touched

upon at the meeting and to place that discussion within the context of papers published during the last three decades.

But first let’s go back thirty years to 1981: The basic theorems of density functional theory (DFT) [2–4] were already established. These theorems permit a calculation of the ground-state density and energy of many electrons in the presence of a static external scalar potential, and thus a prediction of the structure of atoms, molecules, and solids, using fictitious one-electron wavefunctions or Kohn-Sham orbitals [3] that see a self-consistent scalar potential. In practice, the many-body exchange-correlation contribution to the energy as a functional of the density must be approximated, and the only approximation in use then was the local spin density approximation (LSDA) [1, 3, 5, 6]

$$E_{xc}^{LSDA} = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{unif}(n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})), \quad (1)$$

where $\epsilon_{xc}^{unif}(n_{\uparrow}, n_{\downarrow})$ is the exchange-correlation energy per particle of an electron gas with uniform spin densities. The exchange-correlation energy is a relatively small part of the total energy, but it is “nature’s glue”. Without it, bonds would be much longer and weaker than they actually are [7]. LSDA was exact by construction for uniform or slowly-varying densities, but it made serious errors (e.g., energies several eV too high) for the hydrogen atom and other one-electron densities. Thus density functional theory was already widely used in solid state physics, but hardly at all in chemistry [8]. The derivative discontinuity of the energy was not yet known. But it [9] and the generalized gradient approximation (GGA) [10–14]

$$E_{xc}^{GGA} = \int d^3r n(\mathbf{r}) \epsilon_{xc}^{GGA}(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}) \quad (2)$$

were almost ready to appear.

After 1981, two roads diverged in density functional theory. The road subsequently more traveled led from LSDA to GGA and higher-level semilocal functionals (meta-GGAs) [15, 16] and eventually made DFT widely useful to chemists as well as solid state physicists. The road subsequently less traveled led from LSDA to the self-interaction correction (SIC) to the derivative discontinuity (and perhaps to the related LDA+U method [17]), and to a useful treatment of strongly-correlated materials such as transition-metal oxides, lanthanides, and actinides. Curiously, the strengths and weaknesses of these divergent approaches are complementary: The semilocal functionals can be accurate for *sp* bonds near equilibrium, while SIC can be accurate for open-shell *d* or *f* electrons or for any stretched bonds over which electrons are shared. Stretched bonds occur for example in the approach to the dissociation limit [9, 18–20], and also at the transition states that determine the barrier heights for chemical reactions [21]. Perhaps these two roads can converge in a way that will retain the strengths and eliminate the weaknesses of each. But little of this was anticipated in 1981.

First separately [22, 23] and then together [1, 24], Perdew and Zunger proposed to make DFT exact for any one-electron density through an orbital-by-orbital self-interaction correction (PZ-SIC). Their comprehensive paper [1] has been cited over 9000 times, partly for SIC and partly for its parametrization of $\epsilon_{xc}^{unif}(n_{\uparrow}, n_{\downarrow})$. It is the 8th most-cited physics paper of the past 30

years [25]. The conference organizers provided a birthday cake, with the first page of the paper printed on top, giving John Perdew and Alex Zunger a chance to eat their own words, along with the other participants.

2 SIC theory and its formal properties

The PZ-SIC [1] to any density functional approximation is

$$E_{xc}^{PZ-SIC} = E_{xc}^{approx}[n_{\uparrow}, n_{\downarrow}] - \sum_{\alpha\sigma} \{U[n_{\alpha\sigma}] + E_{xc}^{approx}[n_{\alpha\sigma}, 0]\}. \quad (3)$$

Here $\sigma = (\uparrow, \downarrow)$ is the quantum number for the z-component of electron spin, and α is the set of orbital quantum numbers other than spin.

$$n_{\alpha\sigma}(\mathbf{r}) = f_{\alpha\sigma} |\psi_{\alpha\sigma}(\mathbf{r})|^2 \quad (4)$$

is the contribution to the density from normalized orbital $\psi_{\alpha\sigma}(\mathbf{r})$ with fermion occupation number in the range $0 \leq f_{\alpha\sigma} \leq 1$ and

$$n(\mathbf{r}) = n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r}) = \sum_{\alpha\sigma} n_{\alpha\sigma}(\mathbf{r}) \quad (5)$$

is the electron density. Finally

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (6)$$

is the Hartree electron-electron repulsion energy of density n .

PZ-SIC has several correct formal properties [1]. Although it is in a sense an *ad hoc* correction, it is hard to think of any similar approximation for the energy that satisfies so many correct constraints. (There are however reasonable alternatives for the SIC effective one-electron potential, discussed at the conference by Olle Eriksson [26], who focussed on the calculation of the electron density.) Here we will discuss only four correct formal properties, with the fourth only recently appreciated:

1. For any one-electron system in a state $\psi_{\alpha\sigma}$, $n_{\sigma}(\mathbf{r}) = n_{\alpha\sigma}(\mathbf{r})$ and $n_{-\sigma}(\mathbf{r}) = 0$ so

$$E_{xc}^{PZ-SIC} = -U[n_{\alpha\sigma}] \quad (7)$$

to properly cancel the Hartree energy $U[n]$. Thus PZ-SIC is exact by construction for any one-electron density.

2. Any self-interaction correction to the exact functional would be spurious. PZ-SIC seems to give no correction to the exact spin density functional $E_{xc}^{exact}[n_{\uparrow}, n_{\downarrow}]$, since

$$U[n_{\alpha\sigma}] + E_{xc}^{exact}[n_{\alpha\sigma}, 0] = 0. \quad (8)$$

A subtlety here is that, in any system of more than two electrons, some real orbitals necessarily have nodes and are not one-electron ground states for any smooth potential (although they may be ground states for sufficiently singular potentials). We will discuss this further in Sec. 4.1.

3. In a single-center system such as an atom, the PZ-SIC orbitals could be very close to Kohn-Sham orbitals. But, in multi-center systems with the same Kohn-Sham potential on each center, the Kohn-Sham (canonical) orbitals become more diffuse as more centers are added. The PZ-SIC correction on Kohn-Sham orbitals would be non-zero for one atom, but zero per atom for a collection of infinitely-many well-separated identical atoms, and the SIC energy would not be size-consistent. To achieve size-consistency, the energy-minimizing SIC orbitals must localize around each center. This tends to be the case, at least when SIC is applied to LSDA, since in this case the correction tends to be more negative for a more localized orbital. Thus SIC steps outside the Kohn-Sham theory on which it is based. When applied to a uniform electron gas [27–29], the best situation for PZ-SIC-LSDA would be weak localization of the orbitals: weak enough to hardly change the LSDA bulk energy (correct for these densities), but not so weak as to produce a false surface energy (a kind of size inconsistency) [30]. We will discuss size-consistency again in Sec. 5.
4. E_{xc}^{PZ} includes the full Hartree self-interaction correction,

$$- \sum_{\alpha\sigma} U[n_{\alpha\sigma}] \quad (9)$$

as in Hartree-Fock theory and self-interaction-free Hartree theory, and in fact this is its only fully nonlocal term when E_{xc}^{approx} is local (LSDA) or semilocal (GGA or meta-GGA). We will also discuss this correct formal property further in Sec. 2.5.

The orbitals that locally minimize the SIC total energy, subject only to the constraint of orbital normalization, are self-consistent solutions of the equation [1, 24]

$$\left[-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + u([n]; \mathbf{r}) + v_{xc,\sigma}^{approx}([n_{\uparrow}, n_{\downarrow}]; \mathbf{r}) + \Delta v_{xc,\alpha\sigma}^{SIC}(\mathbf{r})\right]\psi_{\alpha\sigma}(\mathbf{r}) = \epsilon_{\alpha\sigma}\psi_{\alpha\sigma}(\mathbf{r}), \quad (10)$$

where $v_{ext}(\mathbf{r})$ is the external potential (typically the attractive interaction between an electron and the nuclei),

$$u([n]; \mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} \quad (11)$$

is the Hartree electrostatic repulsion potential from the electron density $n(\mathbf{r})$, $v_{xc,\sigma}^{approx} = \delta E_{xc}^{approx} / \delta n_{\sigma}(\mathbf{r})$ is the Kohn-Sham exchange-correlation potential of the uncorrected approximation, and

$$\Delta v_{xc,\alpha\sigma}^{SIC}(\mathbf{r}) = -\{u([n_{\alpha\sigma}]; \mathbf{r}) + v_{xc,\uparrow}^{approx}([n_{\alpha\sigma}, 0]; \mathbf{r})\} \quad (12)$$

is the SIC correction to the exchange-correlation potential. Up to this point, we use the same notation $\psi_{\alpha\sigma}(\mathbf{r})$ for all orbitals, but we shall later introduce $\phi_{i\sigma}(\mathbf{r})$ to distinguish SIC localized orbitals from canonical or symmetry-adapted orbitals. Originally Perdew and Zunger [1] were able to solve Eq. (10) only for atoms, where the SIC orbitals are necessarily localized and nearly orthogonal. These early tests suggested that PZ-SIC-LSDA was a nearly ideal approximation, with greatly improved total and ionization energies, more physical orbital energies approximating minus the electron removal energies, proper stability for negative ions [31], correct long-range behavior ($-\frac{1}{r}$) of the exchange-correlation potential, etc.

2.1 Dissociation limit and fractional occupation

One can evaluate the total energy of an atom (or other many-electron system) as a function of the non-integer average electron number in it by using non-integer occupation $f_{\alpha\sigma}$ for the highest-energy partially-occupied orbital. Perdew and Zunger [1] observed that within SIC the total energy varies almost linearly between adjacent integer electron numbers, with slope changes at the integers. In contrast, within LSDA the total energy varies more quadratically, with small or zero slope changes at the integers. The smooth energy variation within LSDA was expected, on the basis of arguments by Slater [32], to lead to spurious fractional-charge dissociation of chemically-distinct atoms in most cases, an effect recently confirmed [18,33]. On the other hand, the piece-wise linear variation suggested by SIC leads to dissociated atoms that are properly charge-neutral.

Thus an approximation, PZ-SIC, led to the exact density functional theory [9] for an isolated open system of fluctuating electron number, in which the energy is exactly piece-wise linear between integer numbers. The nearly-correct behavior within SIC is now known to be what makes PZ-SIC useful for strongly-correlated systems, where electrons are shared between localized orbitals on different sites. And it is also known that property 4 in Sec. 2 is largely responsible for making PZ-SIC nearly many-electron self-interaction free in this sense.

Aron Cohen talked about the difficulty of achieving many-electron self-interaction freedom and accurate static correlation from the same approximate energy functional, using stretched H_2^+ and stretched H_2 as paradigm examples [34].

2.2 Localized and canonical orbitals

Molecules are much more challenging to SIC than atoms. Thus, thinking about applications to molecules allowed one to confront technical and conceptual challenges which arise in orbital-dependent functionals. The solutions of Eq. (10), which are nearly orthogonal in atoms, are no longer so in molecules. Pederson, Heaton and Lin [35, 36] (the Wisconsin group) found a way to implement PZ-SIC-LSDA for molecules, with the constraint of orbital orthogonality, and introduced the terminology of localized and canonical orbitals within PZ-SIC-LSDA [36–38]. The method was also used to determine slight improvements in atoms. An application of the variational procedure, with the constraint of orbital orthonormality, leads to the immediate

conclusion that each of the orbitals which minimize the total energy does indeed move in an orbital-dependent Hamiltonian. However, the orthonormality constraints lead to a more complicated set of Schrödinger-like equations with a set of hermitian off-diagonal Lagrange multipliers coupling the states on the right-hand side of the equation. Several related questions raised within Ref. [1] or shortly thereafter in Refs. [35, 36] pertained to: (i) ensuring orbital orthonormality, (ii) ensuring hermicity of the Lagrange-multiplier matrix, (iii) determining which unitary transformation on a trial set of orbitals was best for constructing the SIC functional, and (iv) finding an interpretation for the Lagrange-multiplier matrix.

The physical answer to these riddles was alluded to by Perdew and Zunger in their original paper when they noted that the optimal orbitals for SIC might resemble the energy-localized orbitals of Edmiston and Ruedenberg [39]. Also, Harrison, Heaton and Lin had already demonstrated that Wannier functions, rather than, Bloch functions lead to self-interaction corrections in insulators of similar magnitude as found in atoms [40]. Following up on this hint, Pederson *et al* [35, 36] took a closer look at the variational procedure and determined that the orbitals which minimize the energy in orbital-dependent theories must also satisfy additional constraints given by:

$$\left[-\frac{\nabla^2}{2} + v_{ext}(\mathbf{r}) + u([n]; \mathbf{r}) + v_{xc,\sigma}^{approx}([n_\uparrow, n_\downarrow]; \mathbf{r}) + V_{xc,i\sigma}^{SIC}(\mathbf{r})\right]\phi_{i\sigma}(\mathbf{r}) = \sum_j \lambda_{ij}^\sigma \phi_{j\sigma}(\mathbf{r}), \quad (13)$$

$$\langle \phi_{i\sigma} | V_{xc,i\sigma}^{SIC} - V_{xc,j\sigma}^{SIC} | \phi_{j\sigma} \rangle = 0, \quad (14)$$

$$V_{xc,i\sigma}^{SIC}(\mathbf{r}) = -\left\{ \int d^3r' \frac{|\phi_{i\sigma}(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} + v_{xc\uparrow}^{approx}(|\phi_{i\sigma}|^2, 0; \mathbf{r}) \right\}. \quad (15)$$

In the original work they suggested that a reasonable name for Eq. (14) was the localization equation since it rhymed, since it philosophically embodied earlier Hartree-Fock-based perspectives offered by Edmiston and Ruedenberg, and since orbitals that satisfied this equation and minimized the total energies for the LSDA exchange-only functional tended to be localized. By 1986, Pederson had already wondered whether he should have called this equation the orbital optimization equation, a name that would have more aptly provided an umbrella for the discussion about intermediate range and complex orbitals at the meeting.

While the above equations first appeared as a departure from the normalization-only equations derived by Perdew and Zunger, it was realized quickly that, if the above equations were solved, a set of orthonormal eigenfunctions of the occupied-orbital Lagrange-multiplier matrix would satisfy an equation identical to Eq. [10] with a generalized nonlocal SIC potential defined according to:

$$\Delta v_{xc,\alpha\sigma}^{SIC}(\mathbf{r})|\psi_{\alpha\sigma}\rangle \rightarrow \Delta V_{xc,\alpha\sigma}^{SIC}|\psi_{\alpha\sigma}\rangle = \sum_i M_{\alpha i}^\sigma V_{xc,i\sigma}^{SIC}(\mathbf{r})\phi_{i\sigma}(\mathbf{r}). \quad (16)$$

In the above expression, the matrix $M_{\alpha i}^\sigma$ is a unitary matrix connecting the localized-orbital set $\{\phi_{i\sigma}\}$ to the so-called canonical orbital set $\{\psi_{\alpha\sigma}\}$. For example (assuming that the SIC correction to the energy is negative for the localized orbitals):

1. For molecules, the matrix M in Eq. (16) connects symmetry-adapted molecular orbitals to orbitals that are qualitatively similar to those of Edmiston and Ruedenberg.
2. For atoms, the matrix M connects s , p and d orbitals to hybridized orbitals.

3. For crystals, the matrix M is simply the unitary matrix which connects Wannier functions to Bloch functions, but the Wannier functions will resemble the atomic localized orbitals (i.e. $M_{\mathbf{k}\mathbf{R}_\nu} \rightarrow \frac{1}{\sqrt{N}}e^{i\mathbf{k}\cdot\mathbf{R}_\nu}$).

Chemistry and chemical physics are games of kcal/mole and any nonsystematic uncertainties due to the use of approximate local orbitals could significantly impact binding energies and barriers. Moreover the determination of ground-state geometries and critical points associated with transition states and reactant/product states essentially requires a capability for the treatment of Hellmann- Feynman forces which, in their derivation, require that all first variations are zero. If a new generation of scientists decides to navigate the “road less traveled” and seek a new rung of orbital-dependent SIC functionals, it is likely that such functionals will be more easily analyzed and constructed if full attention to the variational principle and localization equations is an integrated component during the development of the functionals. However, such a strategy was not historically possible.

2.3 Koopmans’ theorem for SIC

The justification for arguing that it made sense to diagonalize the resulting Lagrange-multiplier matrix came by proposing that of all (e.g., infinite number) the possible unitary transformations one can imagine, there is one unitary transformation that is best from the standpoint of simultaneously minimizing the energy of the N and $N-1$ electron states [36–38]. In this regard, one writes the occupation-dependent localized orbitals in terms of an alternative set of occupation-dependent orbitals and introduces the constraint that the latter set must lie in the space spanned by canonical orbitals of the N -electron system.

$$\phi_{i\sigma}(\mathbf{f}) = \sum_{\alpha} (U_{\alpha i}^{\sigma})^* \sqrt{f_{\alpha\sigma}} \psi_{\alpha\sigma}(\mathbf{f}). \quad (17)$$

It is then determined that the unitary transformation U in the above equation that minimizes the energy for the $N-1+f_{N\sigma}$ is identically equal to the hermitian conjugate of the matrix M in Eq. (15).

This Koopmans-like argument generalized the original arguments of Perdew and Zunger and led to similar numerical results for atoms. However, it provides better approximations to ionization energies in delocalized systems where the lowest ionized state is generally achieved through the removal of a delocalized (canonical) rather than a localized electron. A lingering question that hopefully will be answered some day was raised in Pederson’s talk: Will the generalization for constructing localized orbitals for non-integer systems always lead to fully occupied localized orbitals for integer systems? The propensity of SIC to variationally disallow fractionally occupied solutions to integer systems leads one to expect that an additional constraint is unnecessary, but some effort toward understanding that point would be useful.

We mention that a recent paper by Stengel and Spaldin [41] analyzed Janak’s argument [42] within the context of an application of SIC to crystalline silicon. The authors considered the consequences of assuming that the occupation numbers are to be placed on Wannier functions. The authors noticed that Janak’s theorem is applicable for each Wannier function but that this does not lead to a band structure. This statement is correct regardless of whether one

is finding the Wannier functions that minimize the SIC-LSDA-based or LSDA-based energy functional. Here we reiterate that Koopmans' theorem [36–38] points directly to eigenvalues of the Lagrange multiplier matrix because it picks out the representation of wavefunctions that are most likely to minimize the ionized state and because, within SIC-LSDA, the non-Koopmans' corrections are small. Originally, Janak's theorem was tacitly aimed at the highest-occupied or lowest-unoccupied orbital in the LSDA method. Because of that assumption, the question as to whether or not the resulting derivative had an extremal property was not specifically addressed but seems to have been assumed. For example this theorem was used to argue that, in LSDA, the only fractionally occupied states could be at the Fermi level.

In retrospect, Koopmans' theorem for SIC is stating that the total derivative of the energy with respect to occupation number is equal to the partial derivative of the energy with respect to occupation number (Janak's theorem) if, for that occupation number, the energy is minimized with respect to every other possible variational parameter in the problem (i.e., all other partial derivatives are zero). In other words the Koopman's theorem is very similar to a Hellmann-Feynman theorem for occupation numbers. The original Koopmans theorem [43], for Hartree-Fock theory, is mathematically stronger as it does not rely upon derivatives of the N-electron state to estimate the energy of the (N-1)-electron state. However Koopmans' theorem for SIC includes correlation so it may be physically and chemically stronger.

The Wisconsin SIC group suggested several possible means for representing the nonlocal SIC potentials in terms of local potentials. Such approximations are fine if one is primarily interested in understanding spectra and band alignments, since these approximations allow for SIC calculations with complexity similar to LSDA. However in an era where gradient algorithms [44] and Car-Parrinello methods [45] have become a common means for solving the Schrödinger equation, it seems that methods based upon iterative refinement of the localized orbitals are probably the best approaches. It was also evident at the meeting that the use of SIC had migrated into most types of electronic structure codes. Axel Svane discussed the implementation of SIC into the LMTO methods and described applications to *f*-electron systems. Eric Suraud [46, 47] presented interesting results on an SIC-based approach that is available in the Amsterdam density-functional codes. In this method one uses a common SIC potential for an N-electron system based upon the average orbital density ($n(\mathbf{r})/N$). For example when the method is applied to sodium clusters, the authors of Refs. [46, 47] find that the one-electron ionization energy computed using a total-energy difference agrees well with the highest-occupied orbital eigenvalue. The averaged SIC potential was approximated as:

$$\Delta v_{xc,\alpha\sigma}^{AVG-SIC}(\mathbf{r}) = -\{u([n/N]; \mathbf{r}) + v_{xc,\uparrow}^{approx}([n(\mathbf{r})/N, 0]; \mathbf{r})\}. \quad (18)$$

Such an approach eliminates the need to solve localization equations, at the expense of a more approximate SIC potential. This approach provided good valence ionization energies and is also exact in the one-electron limit. In scheduled talks and informal discussions, the Icelandic group (Peter Klüpfel, Simon Klüpfel, Hildur Guðmundsdóttir, and Hannes Jónsson) shared their experiences with several different strategies for finding solutions to the SIC equations, including an early method due to Goedecker and Umrigar [48].

Another form of self-interaction correction [49–52] that was based on the use of pseudopotentials

received a significant amount of discussion in the talks. In this approach, atomic corrections are performed to determine nonlocal, norm-conserving pseudopotentials which incorporate self-interaction corrections in a nonlocal l -dependent pseudopotential. Once this method is adopted, the nonlocality of the pseudopotential allows for the calculations of self-interaction corrections in condensed systems. Bjoern Baumeier described this method for calculations of electronic structures in solids. This method was used for calculations on a large number of compounds with partially ionic characteristics. Materials included silicon carbide and alkali-metal oxides. Calculated properties included electronic and atomistic structures and optical spectra. The method was also shown to be useful for the study of magnetic properties of dilute magnetic semiconductors. Alessio Filippetti discussed use of this approach for the study of strongly-correlated oxides. Hisazumi Akai discussed an approximate SIC method for the Kohn-Korringa-Rostocker methodology and provided a variety of applications. Stephano Sanvito also used this pseudopotential approach in his discussion on transport properties.

Nikitas Gidopoulos suggested a possibly unique way to turn an approximate Kohn-Sham potential into a self-interaction-free Kohn-Sham potential (multiplicative and orbital-independent) [53].

2.4 Spectra and excitations within SIC

The qualitative differences between SIC and SIC-LSDA are depicted in Fig. 1. The SIC pulls down the occupied states relative to the unoccupied states which generally leads to a gap (Γ) that is improved in comparison to experiment. Localized excitations in a vacuum or excitons in a wide-gap insulator (depicted as E) can be difficult to identify within LSDA calculations. In LSDA-SIC, with an approximation to the particle-hole interaction (δ), the description of such excitations can be improved. For defects in solids, where localized levels occupy the gap, LSDA and GGA calculations tend to place the defect levels (labeled by Δ) too close to, or overlapping, with the unoccupied conduction band. However, SIC-LSDA pulls the defect levels down and often places the LSDA-false-positive shallow levels (discussed in Alex Zunger’s talk) in the proper location. With inclusion of SIC and a particle-hole interaction, an unoccupied continuum of defect levels, predicted by the Mott-Gurney theorem, begins to emerge [54]. Less consensus exists regarding the differences between SIC-LSDA and LSDA for charge-transfer excitations, but there are some examples that show LSDA can dramatically underestimate these energies and that an approximate self-interaction-corrected energy with a particle-hole interaction restores the correct asymptotic form for donor-acceptor and other charge-transfer excitations. For example, in a vacuum, these energies are found to be close to $(I-A-1/R)$ [55,56]. For spin excitations, determined from LSDA/GGA derivations of Heisenberg Hamiltonians, a large number of calculations show that the spin-excitation energies are overestimated due to LSDA’s tendency to slightly delocalize the d -electrons and since the kinetic exchange interactions depend exponentially on the localization of the d -electrons. Therefore inclusion or partial inclusion of self-interaction corrections lowers the spin-excitation energies (See Ref. [57] and references therein) and improves agreement with experiment. While not depicted in the picture, vibrational spectra [58,59] seem to be relatively well accounted for within LSDA and GGA. However, since polarizabilities are dependent on SIC [20], the Raman intensities are also expected to show some dependence on the

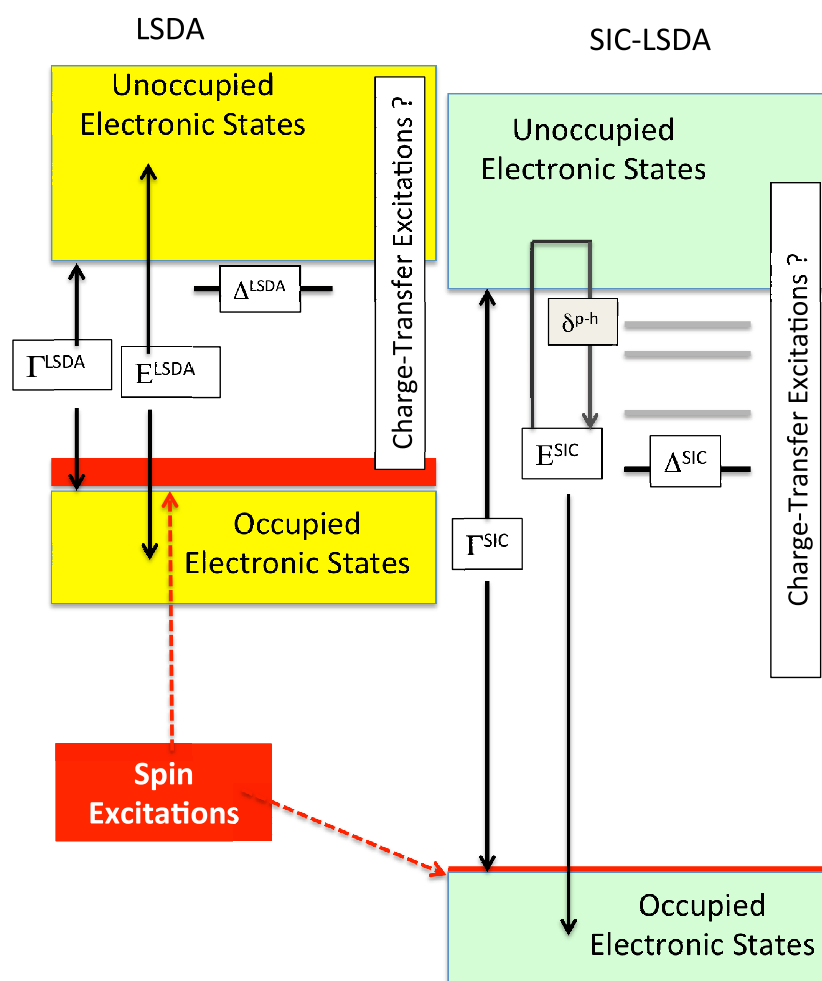


Figure 1: Schematic and qualitative picture depicting differences between LSDA (superscript “LSDA”) and SIC-LSDA (superscript “SIC”) energy levels. The behavior of the energy gap, excitonic states, and defect levels are depicted by Γ , E , and Δ respectively. The particle-hole interaction is depicted by δ^{p-h} . The behavior of the very low-energy spin excitations are depicted in red (not to scale). There is some evidence that charge-transfer excitations are also improved within SIC-LSDA. SIC may be expected to decrease the occupied bandwidth in wide-gap systems and increase the occupied bandwidth in gapless systems. The picture is expected to inform one’s intuition and apply to many cases.

inclusion of self-interaction corrections. From this standpoint we note that Delugas, Fiorentini and Filippetti have found that dynamical charges are improved by approximately 15 percent in LaAlO_3 [60].

Exact accounting for the changes to the variational principle due to explicit orbital dependence is not likely to be of significant import from the standpoint of the calculation of electronic spectra. This seems to have been highlighted in the earlier works of Harrison *et al* [61] and in much of the f -electron calculations that have been led by Temmerman *et al* [62–64].

At the meeting Eric Suraud discussed the use of an average-SIC approach for the calculation of radiative transitions using the Amsterdam codes. Good agreement for valence ionization energies was obtained. Similarly Takao Tsuneda showed that a regional self-interaction correction seemed to give good agreement for core-level spectroscopy. Stephan Kuemmel discussed a means for determining the shape of the frontier orbital through the time evolution of the SIC-LSDA solutions, and compared SIC predictions to “measured orbital densities” [65]. Also in this talk, a summary of earlier SIC-LSDA work which addressed its relevance to energy and charge transfer was provided [66].

Julie Staunton discussed the calculations of magnetic properties within an *ab initio* method [67–69]. She provided a brief overview of the disordered local moment (DLM) method of Lueders *et al* for incorporating effects of strong electron correlations using a local-SIC formulation. Applications to the phase diagram of Gd were presented. Additional calculations on transition-metal oxides (MnO, FeO, CoO and NiO) were presented. These materials have anti-ferromagnetic order at low temperature, and the DLM-SIC approach explained the persistence of the large insulating gap into the paramagnetic state.

Molecular magnets [57, 70] represent another area where self-interaction corrections can be important, particularly in the Ni and Fe-based systems. For the $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{C}_6\text{H}_{15}\text{N}_3)_6\text{Br}_6]^{2+}$ molecule [70], density functional theory with the PBE-GGA functional describes the electronic structure of the molecular solid well, as evidenced by detailed comparison of the calculated optical spectrum with experiment. However, the HOMO-LUMO gaps are consistently underestimated and the calculations of the magnetic anisotropy Hamiltonian in this “ Fe_8 molecule” are significantly less reliable than for molecular magnets composed of other $3d$ -elemental centers [57]. The underestimation of the gap and/or the slight delocalization of the metal $3d$ electrons could be fixed through the inclusion of SIC and may provide more accurate calculations of spin-Hamiltonians and magnetic-anisotropy Hamiltonians.

Harrison *et al* [71] have presented empirical evidence that, for atomic excitations, one can determine excitation energies by allowing the unoccupied levels to move in the same SIC potential as the hole electron. A justification for this procedure based upon variationally optimized orthogonalized excited states has been offered for localized systems [54] and shown to provide very good quantitative results for F-centers in LiF. More recently Baruah and Pederson have extended these arguments to address a calculation of the charge-transfer excitation in a large molecular triad [55] composed of a C_{60} molecule and a carotenoid organic chain that are tied together by a porphyrin chromophore. Without the explicit constrained variational procedure with orthogonalized ground and charge-transfer states, the LSDA-based charge-transfer excitation would collapse into a delocalized state with an energy that significantly underestimates experiment.

2.5 Bond energies and relation to GGA's

The GGAs, which started to appear in the 1980s, gave a much bigger improvement to atomization energies [10–12, 14] than PZ-SIC-LSDA did. GGAs, meta-GGAs [15, 16], and hybrids of these semilocal functionals with exact exchange made density functional theory popular in chemistry from the 1990s to the present. SIC was largely forgotten, except by a community of solid state physicists interested in studying strongly-correlated oxides (well-represented at the conference) and by a few chemists, e.g. [72–75].

In 2004-2005, Vydrov and Scuseria [76, 77] implemented a version of self-consistent PZ-SIC-LSDA with orbital orthogonality into a developmental version of the Gaussian code. They then applied it to a large test set of molecules. They found that the energy barriers to chemical reactions (stretched-bond situations) were improved significantly over LSDA, as Patchkovskii and Ziegler [21] had found before. But the results for equilibrium properties were disappointing: Atomization energies were only slightly improved over LSDA, and bond lengths were actually worsened.

One might expect better results from applying PZ-SIC to more sophisticated semilocal functionals like GGA or meta-GGA, but the opposite is found. Vydrov *et al.* [78] argued that GGAs and meta-GGAs improve E_{xc} over LSDA for smooth, nodeless densities, but not for oscillating and noded orbital densities, where the relative density-insensitivity of LSDA may actually be an advantage. They also proposed a scaled-down SIC that is still exact for all one-electron densities but scales down the self-interaction correction in many-electron regions. They found that this improved equilibrium properties over the original PZ-SIC, but worsened stretched-bond properties. By losing the correct formal property 4 of Sec. 2, they also lost the correct many-electron self-interaction freedom [19, 79], retaining only one- and two-electron self-interaction freedom [19].

3 SIC for localization-delocalization transitions in solids and molecules

The explicit appearance of the orbital densities in the SIC formalism provides for greater computational challenges but also provides a richer space of physical and chemical solutions. The richness or multifaceted solutions offered by the inclusion of SIC were highlighted in several talks at the meeting. Alex Zunger's title, abstract, and talk succinctly, precisely and humorously framed the problem. Alex referred to the systematic exaggeration of delocalization as one of the primary "tragedies" faced by DFT practitioners. He spoke of this problem in terms of defects in insulators, particularly in regard to ZnO and GaAs, and the challenge of polarons [80, 81]. He expressed hope that a functional that could reproduce the near-linear dependence on occupation number that is found in SIC-LSDA could enhance further joint collaborative efforts between experimentalists and theorists. Other early works that talked about the important role of self-interactions in defect calculations include [82] and [54]. Here we provide an account on other manifestations of this issue.

3.1 Actinides and materials containing f -electrons

Axel Svane discussed his collaborative work with the Daresbury group on the calculation of phase diagrams of SmS systems [62]. Svane showed for a variety of systems that SIC provided a mixed picture, with some electron states being localized and some being itinerant. Such spectacular phase transitions are observed in cases like elemental Ce, CeP, SmS, and YbS. In actinides this delocalization phenomena proceeds by delocalizing the f -electrons one at a time, and the volume range over which the transition from the localized to the itinerant scenario can be identified

As a function of pressure, the partially filled f -shell must be handled carefully in these systems, as nature can be indecisive about the number of f -electrons that should be fully occupied within the atomic region of the Sm. Axel Svane showed that, depending upon volume, the Sm could accommodate either five or six f -states and that SIC succeeded in determining the parts of volume-space that preferred five rather than six electrons. The conclusion is that the SmX compounds require the self-interaction corrections to describe the filling of the f -shell as a function of unit-cell volume. The calculated SIC phase diagrams of SmS and SmAs compounds are found to be in quantitative agreement with experiment. For the high-pressure phase the results show that the sixth electron is itinerant and chooses to distribute itself amongst the remaining band of partially occupied f -states near the Fermi level. The itinerant states have no SIC. In contrast, the lower-density phase has a total of six f states occupied below the Fermi level.

Klaus Capelle discussed a means for testing the limitations of DFT through the use of model hamiltonians, and tested several versions of SIC within the Hubbard model [83].

3.2 Free-electron gas: dense metallic states and dilute “insulating” states?

As discussed in Refs. [27–29], there have been several different attempts to find localized orbitals for the free-electron gas. Most of the work discussed in these references was in regard to the standard free-electron gas which leads to a set of occupied plane-wave states inside a Fermi sphere. However in Ref. [29], Pederson, Heaton and Harrison also considered a phase of the free-electron gas that was much earlier considered by Wannier when he introduced the functions which bear his name [84]. It is interesting to note that, while Wannier was discussing plane-wave states, the title of that paper was *Structure of Electronic Excitation Levels in Insulating Crystals*. In this paper, Wannier wrote down Wannier functions of the form:

$$\omega(r - R_\mu) = \frac{1}{\sqrt{\pi^3}} \Pi_i \frac{\sin[q_F(x^i - X_\mu^i)]}{\sqrt{q_F}(x^i - X_\mu^i)}, \quad (19)$$

with $\mathbf{R}_\mu = (m_x, m_y, m_z)(\pi/q_F)$ and q_F is half the width of the cubic Brillouin zone. By inscribing the largest possible “Wannier cube” ($q_F = \frac{k_F}{\sqrt{3}}$) within the Fermi sphere, a set of Wannier functions may be derived. This set of functions leads to a negative self-interaction correction for about 37 per cent of the plane-wave states. This leads to a slightly wider occupied density of states which is in better agreement with Hartree-Fock theory. By inspection, and related to the uncertainty principle, it is clear that the original Wannier functions get more localized as the magnitude of the q_F -vector gets larger.

To frame the part of the paper on the insulating free-electron gas within the context of localization-

delocalization transition, we again mention that the Daresbury-Aarhus group has successfully accounted for a high-density to low-density phase transition using SIC. The explanation appears to be that one can fill the Brillouin zone in two different ways. In one case it is possible to transform to six localized orbitals per site and in the other case only five. Now if one creates a “Wannier cube” that is large enough to accommodate all the electrons, q_F gets larger and the Wannier functions become more localized. In addition to the fact that the Wannier functions are more localized, there are now 2.72 times as many localized orbitals. In a nutshell, Ref. [29] put forth the hypothesis that in the low-density limit, despite the large increase in kinetic energy associated with a non-spherical Fermi surface, the derivative of the energy with respect to $n^{1/3}$ is more negative in the limit of $n = 0$ (if the SIC-energy is indeed negative as is the case for the LSDA exchange-only functional). It was shown analytically that, in the low-uniform-density limit, a state that is based on a full band of plane waves/Wannier functions confined within a simple-cubic “Wannier cube” is lower in energy than the standard state composed of plane waves confined to the Fermi sphere. Pederson also speculated that this feature could be related to the Wigner crystallization and estimated that for values of $r_s > 35$ the uniform density “insulating state” (plane waves within a “Wannier cube”) are lower than the metallic state. That paper noted that “the subject of SIC-induced Wigner crystallization of the free-electron gas and antiferromagnetic- paramagnetic transitions in monovalent metals will be explored in a forthcoming paper”, but it has not yet appeared. However in retrospect, it may be very important to ascertain whether there are indeed two quantum-mechanical phases of the uniform electron gas corresponding to two different Brillouin zones and two different density regimes. Knowing this may very well determine if the sign of the SIC-energy of a localized orbital in the low-density limit must be negative. The fact that numerous Brillouin zones (beyond those of Refs. [27–29]) exist means the estimate above is just that.

Based on experience with finding the SIC-LSDA antiferromagnetic solutions in the separated-atom limit for Li_2 [36] molecules, Ref. [29] also mentioned the possibility of finding transitions between antiferromagnetically-ordered and paramagnetic states in monovalent metals, which is related to the discussion of BCC hydrogen presented by Thomas Schulthess. Consensus on what SIC predicts in the exchange-only limit and with correlated functionals for the free electron gas and monovalent n -dimensional systems could provide insight on which path toward improving SIC is likely to be most useful.

3.3 BCC hydrogen

Thomas Schulthess discussed attempts at understanding the localization-delocalization transition in BCC hydrogen and NiO within full-potential methods. For example in very early work by Svane and Gunnarsson [44], it was demonstrated that SIC-LSDA found a metal to antiferromagnetic transition at $r_s = 2.45$. Particular emphasis was on a description for addressing BCC hydrogen and metal-oxides using an implementation of SIC in a LAPW-based method. The previous LMTO-ASA-based investigations [44, 85, 86] were found to be in accord with the results of this more accurate methodology.

3.4 Geometries of radicals

The self-interaction error can also be the cause of qualitatively incorrect structures in organic radicals. For example, very recently Oyeyemi *et al.* [87] have demonstrated this in calculations on the alkynyl radical structure. In this work they demonstrate for a large range of functionals, including hybrids, that the self-interaction error causes an erroneous electron delocalization which induces a rehybridization of the valence electrons and ultimately causes a qualitatively incorrect structure of the radical (bent when it should be linear). Ramifications of such qualitatively incorrect structures then lead to quantitative thermochemical errors.

3.5 Polarizabilities, charge separation and transport

LSDA, GGA, and other semilocal functionals can fail to describe processes in which electrons are transferred over long distances, even in the ground state. Failures in the dissociation limit have already been discussed in Sec. 2.1. The semilocal functionals also overestimate the static polarizabilities, and even more the static hyperpolarizabilities, of molecules, especially for long molecular chains with stretched bonds between the atoms. These errors are largely corrected by PZ-SIC-LSDA [20]. In this reference, the longitudinal polarizabilities were calculated within high-level quantum-chemical methods, with both local and gradient-corrected functionals, and with self-interaction-corrected local and gradient-corrected functionals. The results show small (at most 20 percent) variation between all methods for small H₂ chains but large (50 percent) errors for a chain of six dimers when one compares DFT approximations to any method that accounts for the self-coulomb interaction in some way (e.g., SIC, CCSD, HF, MP4). Such a spurious propensity toward DFT-based dielectric breakdown is a very fundamental issue that is relevant to charge transfer, donor-acceptor systems (especially when in solvents), and molecular electronics.

Nicola Marzari provided a frank and provocative assessment on problems related to localization-delocalization transitions. He commented on the need to include self-interaction corrections and a generalized Koopmans relation [88] to improve the description of a variety of fundamental processes relevant to energy applications. Specific examples mentioned in his talk included charge-transfer excitations, photoemission spectra, and the structure and reactivity of transition-metal complexes. Also related to the proper dissociation of ionic molecules are questions related to simulation of charge transfer that are important for understanding photo-driven solar collection processes and simulation of molecular electronics. Sanvito discussed the prospects for improving the simulation of molecular electronics at the meeting.

Sanvito's contribution discussed the most common pitfalls in the non-equilibrium Greens function (NEGF) DFT approach to electron transport, and demonstrated that an approximate self-interaction correction could be used to obtain quantitative predictions for technologically relevant nano-scale devices. Examples concentrated on transport in molecules, in multi-functional tunnel junctions, and in organic systems in solution.

3.6 Technical details

There is an important technical feature, that received significant hallway discussion, on the use of the unified Hamiltonian and the analysis of the results. We attempt to reproduce that discussion here, as this, and actually all other iterative approaches which successfully minimize the SIC energy, may tempt one to conclude that there are in fact multiple orbital sets and multiple band structures which lead to the exact same total energy and the exact same density. To discuss this in the most efficient manner, it is easiest to first consider the case where the SIC happens to be zero, which would lead to a use of the unified Hamiltonian for a DFT Kohn-Sham calculation. Within density-functional theory, it is easy to verify that unitary transformations on the Kohn-Sham orbitals will allow one to determine an infinite number of orbitals sets that have different nondiagonal Lagrange-multiplier matrices but lead to the same total energy and the same total density. For simplicity we first consider any one of the equivalent sets of DFT orbitals that lead to a set of diagonal elements of the Lagrange-multiplier matrix that are nondegenerate. Using any one of these sets of DFT orbitals for construction and subsequent diagonalization of the unified Hamiltonian will allow us to re-extract the equivalent set of orbitals and the diagonal elements of the Lagrange-multiplier matrix for this set. Of course this set does not agree with the eigenvalues of the DFT Hamiltonian. However diagonalizing the Lagrange-multiplier matrix for this set of orbitals or any other set of unitarily equivalent orbitals will give the exact KS orbitals and the exact KS eigenvalues. Thus even for DFT, if a unified Hamiltonian is used, it is always necessary to diagonalize the Lagrange-multiplier matrix to compare results from different computer codes or users. Different starting points in the iterative procedure will lead to different, but unitarily equivalent, Lagrange-multiplier matrices even for density-functional theory. To the extent that this should happen for DFT, it should not be surprising that orbital-dependent functionals can also converge to different, but unitarily equivalent, Lagrange-multiplier matrices. This is simply a correct aspect of the minimization procedure.

3.7 Bandgaps and localized excitation energies

In insulating and semiconducting solids, LSDA, GGA and meta-GGA orbital energies yield fundamental band gaps that are smaller than experimental values associated with excitation of an electron to the lowest-lying conduction state. It has been argued [89, 90] that, because of the derivative discontinuity, a similar underestimation could occur in the exact Kohn-Sham bandstructure for the neutral solid, in which all electrons see the same multiplicative orbital-independent effective potential. When the electrons are tightly-bound, as in solid Ne, the gap in the exact Kohn-Sham band structure may more accurately approximate the first exciton energy. From the standpoint of comparing results for the occupied orbital space, it is clear that one needs to compare eigenvalues of the Lagrange-multiplier matrix and that the associated eigenfunctions will generally exhibit the point-group and/or translational symmetry of the system in question. However a standard means for comparing unoccupied states may need to be established. The purpose of this section is to provide a discussion on past treatments of unoccupied states in SIC, without claiming that any of these treatments are necessarily rigorous when compared to more modern approaches to excited states. Such a discussion is useful from the standpoint of

developing a standard means for comparison, especially since different methodologies treat the unoccupied states differently. Historically, there were efforts aimed at improving band gaps by allowing the delocalized occupied states to move in their standard SIC potential according to Eqs. (13-17), and to take the point of view that the unoccupied states should simply move in the LSDA hamiltonian. Since a delocalized electron outside a closed shell will have an LSDA eigenvalue that is an excellent approximation to the electron affinity, one may argue that the lowest unoccupied bloch function in a crystal should be a good approximation to the inverse photoemission experiments. Moreover, the Koopmans' theorem tells us that the energy to remove a delocalized electron from the crystal is approximately equal to the highest-occupied eigenvalue. Therefore, at least for ionic insulators, we expect that the eigenvalue differences will agree with SIC-LSDA total energy differences and form a reasonable approximation to one idealization of the experimental band gap. Further it is known that the resulting “scissored” bandstructure when compared to experiment is improved over LSDA [40, 41, 49, 91]. Note that the SIC of a delocalized electron is zero so it will not affect the estimate of an affinity. For lack of a better terminology we refer to this as the SIC insulating bandgap approach (SIBA).

In atoms [61], F-centers [54], other defects [82], core-level-excitations, and (presumably) localized excitons, there is good numerical evidence that one can obtain relatively accurate excitations by allowing the lowest unoccupied “particle” state to move in the same SIC-potential as the “hole” state. Arguments have been made as to why that should be expected [54]. So, for localized excitations and delocalized excitations in wide-gap systems, these two different treatments of the unoccupied states could be used as a basis for comparing SIC results that have been generated using different implementations. Simply examining these approximations will also allow practioners to develop some intuition on what types of interactions are required for better qualitative treatments of excited states.

The more difficult question is to determine a means for comparing gaps in strongly covalent systems. In Ref. [38], Pederson, using the methods described in [92], found, using SIBA, that the resulting silicon bandgap would be overestimated significantly since the SIC shift of a silicon 3s or 3p function (in an atom or in a crystal) is approximately 3.52 eV. If a SIBA picture is adopted, this would lead to a bandgap of approximately 4.22 eV which is in good agreement with the recent calculations of Stengel and Spaldin who find a value of 4.5 eV. [41]. However, in Ref. [38], Pederson argued that one should not expect the SIBA treatment to work for systems, such as silicon, where the excitonic levels lie above the onset of the conduction band.

4 Possible directions for further improvement of SIC

The Perdew-Zunger SIC has had both striking successes and striking failures, as summarized in the preceding sections. “How can anything so right be so wrong?” It is hard to see how to change the form of PZ-SIC without losing at least some of its formally correct properties. But there are two other possibilities that might work together:

4.1 Complex localized orbitals for SIC

PZ-SIC might work much better, and might improve along with the functional E_{xc}^{approx} being corrected, if we could replace the oscillating and noded orbital densities by smooth, un-noded densities. (See point 2 of Sec. 2.) While real orbitals that are orthogonal must have noded orbital densities, complex orbitals need not. For example, plane waves are complex, orthogonal, and have constant orbital densities. Their real and imaginary parts have nodes, but not in the same places. Can we start from real canonical (delocalized) orbitals, then make a unitary transformation [35,36] to localized complex orbitals that lower the SIC total energy more than localized real orbitals do? At the SIC workshop, John Perdew argued that such a transformation might represent a formal improvement to PZ-SIC, while Peter Klüpfel and collaborators demonstrated such a transformation for use in GGA [93].

From a technical point of view it should be noted that the localization equations are ambivalent toward changing the real and imaginary parts of a set of orbitals that already satisfy the localization equations. In other words, if one finds a set of real localized orbitals, an infinitesimal 2x2 complex unitary transformation would not change the energy to first order. So once a set of real localized orbitals are found, one is trapped in that orbital set. To escape that set and consider other possible solutions of the richer space of chemical and physical solutions requires the user to guess a different set of localized orbitals and determine if other local minima provide better estimates to the global SIC state. Alternatively one could consider second derivatives of the localization equations, which are not necessarily zero, to provide insights about whether a set of orbitals corresponds to a global minima. In the absence of an SIC functional for the exchange-correlation term, the second derivatives would provide easily calculated coulomb integrals and essentially determine which set of Edmiston-Ruedenberg orbitals provided globally stable solutions. However the intrinsically non-quadratic behavior of the exchange-correlation part of the functional makes it difficult to gain further insight through such analysis. Kuemmel, during his talk, commented that the time-dependent evolution of the SIC equations, which provides a means for minimizing the energy, necessarily considers the possibility of complex orbitals. Perhaps this approach to orbital localization allows one to circumvent the possibility of being trapped in real solutions or to confirm their global stability.

Additional guidance may be found by reviewing earlier work on atoms that grappled with similar issues on simpler systems. In applications to atoms, Harrison [71] discussed the use of spherical-harmonic p -orbitals and cartesian p -orbitals for construction of the SIC potential, and referred to this as Central-Field Self-Interaction Correction (CFSIC). For Ne, Harrison's work showed that the spherical-harmonic (complex) p -orbitals produced an SIC correction to the total energy that was approximately 2.7 eV lower than the cartesian representation. Further support that a set of complex nodeless wavefunctions would provide more negative SIC energies comes from a wealth of data showing that sphericalized densities lead to even larger (more negative) SIC corrections to the energy. However in Ref. [37], it is shown that by allowing s - p hybridization, referred to as hybridization-localization (HL), the real sp^n hybrids always delivered lower energies for the first 18 atoms in the periodic table. For neon the real HL solution is about 6.0 eV lower than the complex CFSIC solution. Still there is yet one more unpublished "however": For the SIC functional and numerical schemes used in Ref. [37], Pederson's recollection is that a brute-force

determination of the SIC energy using a large series of 2x2 complex unitary transformations on the entire orbital space ($1s, 2s, 2p_x, 2p_y, 2p_z$) did indeed produce complex orbitals with energies slightly lower than the sp^n hybrids.

4.2 Higher l hybrid orbitals

In addition to considering the possibilities of complex localized orbitals, Pederson suggested that, especially for applications which include f -electrons, localizing transformations achieved by “bonding” and “antibonding” combinations of f and d functions (real or complex) need to be considered. Since hybridization of states of different angular momentum and particularly parity occurs naturally in molecular bonds, it immediately follows that ignoring the possibility of localized atomic orbitals that are mixtures of different angular momenta is susceptible to overestimates of the actual SIC bond energies. Interestingly, in applications to the Zn^{2+} cation, Stengel and Spaldin suggest that nine nearly similar sp^3d^5 hybrids could be the best localized orbitals [41].

5 Perspectives

It is also possible that further improvement of GGAs or meta-GGAs could make them work better with PZ-SIC. Orbital densities typically have larger reduced density gradients than total densities do, so they sample more of the large-reduced-gradient behavior of a GGA or meta-GGA. Standard GGAs and meta-GGAs may not be optimally constructed for this sampling. Indeed, the Icelandic group found failures of size-consistency for PZ-SIC applied to the Perdew-Burke-Ernzerhof GGA [14], arising from the strong large-reduced-gradient exchange enhancement over LSDA exchange that makes the PZ-SIC energy correction positive for some localized orbitals. (See point 3 of Sec. 2.) This strong enhancement also leads to an incorrect behavior under non-uniform density scaling to the two-dimensional limit [94–97], so fixing the latter problem might also fix the former. Diminishing the exchange enhancement factor (but in a different way) has already improved GGA [98–100] and meta-GGA [16] performance for solids. Note that many meta-GGA’s including [16,17] are already self-correlation free, so for them one can replace E_{xc}^{approx} by E_x^{approx} in the SIC correction term of Eq. (3).

Perhaps a convergence of “the road more traveled” with “the road less traveled” would provide an optimal unified nonempirical solution for the problems of “weak correlation” and “strong correlation”. The hybrid functionals [101–104] that mix fractions of semilocal and exact exchange achieve this to some extent, but not fully and with the help of one or several more-or-less empirical parameters. Or perhaps the solution will come from a combination of the full exact exchange energy with some compatible nonlocal correlation energy functional, constructed using the exact exchange energy density and the sum rule on the correlation hole around an electron, as discussed at the conference by Adrienn Ruzsinszky. Such methods would appear to keep the important corrections for self-interaction error but leave the computational complexities of the localization-equation-induced undergrowth behind.

Robert Frost was known to warn his audience that *The Road Not Taken* is a “tricky poem” inspired by a hiker’s concern that there was always a potentially better path to try. Unlike quantum particles, quantum physicists can not try all paths. It is expected that the optimal combination of the “road less traveled” with the “road more traveled” will in itself present many more different and exciting paths to explore and that the analysis leading to that optimal combination may be as tricky as the analysis of the poem. However, if scientific citation statistics [1,25] are a guide, the end of this chapter should read:

I shall be telling this without a Ψ
Somewhere ages and ages hence:
Two roads converged in a green wood, and why?
This made the one best traveled by,
And that has made all the difference. [*sic*]

6 Acknowledgments

JPP acknowledges support from the National Science Foundation under Grant No. DMR-0854769 and under Cooperative Agreement No. EPS-1003897 with support from the Louisiana Board of Regents. Both authors thank the organizers, speakers, and participants for an interesting and stimulating conference. MRP thanks Prof. Chun C. Lin for providing the requisite “initial conditions” for part of this workshop report which allowed him to collaboratively focus on a hard and relevant problem for four stimulating years. The discussion does not necessarily represent the priorities of any government agency.

References

- [1] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- [2] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- [3] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
- [4] M. Levy, Proc. Nat. Acad. Sci. (USA) **76**, 6062 (1979).
- [5] U. von Barth and L. Hedin, J. Phys. C: Solid State Phys. **5**, 1629 (1972).
- [6] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
- [7] S. Kurth and J.P. Perdew, Int. J. Quantum Chem. **77**, 814 (2000).
- [8] R.O. Jones, “Density functional theory: a personal view”, in *Strongly Correlated Systems*, eds. A. Avella and F. Mancini, Springer Series in Solid State Physics **171**, 1 (2012).
- [9] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz, Phys. Rev. Lett. **49**, 1691 (1982).
- [10] D.C. Langreth and M.J. Mehl, Phys. Rev. B **28**, 1809 (1983).

- [11] J.P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).
- [12] A.D. Becke, Phys. Rev. A **38**, 3098 (1988).
- [13] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- [14] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- [15] J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
- [16] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, and J. Sun, Phys. Rev. Lett. **103**, 026403 (2009).
- [17] M. Cococcioni and S. de Gironcoli, Phys. Rev. B **71**, 035105 (2005).
- [18] A. Ruzsinszky, J.P. Perdew, G.I. Csonka, O.A. Vydrov, and G.E. Scuseria, J. Chem. Phys. **125**, 194112 (2006).
- [19] A. Ruzsinszky, J.P. Perdew, G.I. Csonka, O.A. Vydrov, and G.E. Scuseria, J. Chem. Phys. **126**, 104102 (2007).
- [20] A. Ruzsinszky, J.P. Perdew, G.I. Csonka, G.E. Scuseria, and O.A. Vydrov, Phys. Rev. A **77**, 060502 (2008).
- [21] S. Patchkovskii and T. Ziegler, J. Chem. Phys. **116**, 7806 (2002).
- [22] A. Zunger and M.L. Cohen, Phys. Rev. B **18**, 5449 (1978).
- [23] J.P. Perdew, Chem. Phys. Lett. **64**, 127 (1979).
- [24] A. Zunger, J.P. Perdew, and G.L. Oliver, Solid State Commun. **34**, 933 (1980).
- [25] For a table of the 18 most-cited physics papers 1981-2010, see <http://tulane.edu/sse/pep/> under Department News. Note that 10 of the 18 are DFT papers.
- [26] U. Lundin and O. Eriksson, Int. J. Quantum Chem. **81**, 247 (2001).
- [27] R.A. Heaton, J.G. Harrison, and C.C. Lin, Solid State Commun. **41**, 827 (1982).
- [28] M.R. Norman, Phys. Rev. B **28**, 3585 (1983).
- [29] M.R. Pederson, R.A. Heaton, and J.G. Harrison, Phys. Rev. B **39**, 1581 (1989).
- [30] J.P. Perdew, "Size-Consistency, Self-Interaction Correction, and Derivative Discontinuity", in *Density Functional Theory of Many-Electron Systems*, edited by S.B. Trickey, Advances in Quantum Chemistry **21**, 113 (1990).
- [31] L.A. Cole and J.P. Perdew, Phys. Rev. A **25**, 6291 (1982).
- [32] J.C. Slater, *The Self-consistent Field in Atoms, Molecules, and Solids*, McGraw-Hill, New York, 1974.

- [33] A.D. Dutoi and M. Head-Gordon, Chem. Phys. Lett. **422**, 230 (2006).
- [34] A.J. Cohen, P. Mori-Sanchez, and W. Yang, Science **321**, 792 (2008).
- [35] M.R. Pederson, R.A. Heaton, and C.C. Lin, J. Chem. Phys. **80**, 1972 (1984).
- [36] M.R. Pederson, R.A. Heaton, and C.C. Lin, J. Chem. Phys. **82**, 2688 (1985).
- [37] M.R. Pederson and C.C. Lin, J. Chem. Phys. **88**, 1807 (1988).
- [38] M.R. Pederson, "Orbital Dependent Improvements of the Density Functional Formalism with Applications to Atoms, Molecules and Crystalline Silicon", Thesis, University of Wisconsin - Madison (1986).
- [39] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963).
- [40] R.A. Heaton, J.G. Harrison and C.C. Lin, Phys. Rev. B **28**, 5992 (1983).
- [41] M. Stengel and N. A. Spaldin, Phys. Rev. B **77**, 155106 (2008).
- [42] J.F. Janak, Phys. Rev. B **18**, 7165 (1978).
- [43] T. Koopmans, Physica **1**, 104 (1934).
- [44] A. Svane and O. Gunnarsson, Solid State Comm. **76**, 851 (1990).
- [45] T.D. Kühne, M. Krack, F.R. Mohamed, and M. Parrinello, Phys. Rev. Lett. **98**, 066401 (2007).
- [46] J. Messud, P.M. Dinh, P.-G. Reinhard, and E. Suraud, Phys. Rev. Lett. **101**, 096404 (2008).
- [47] J. Messud, P.M. Dinh, P.-G. Reinhard, and E. Suraud, Ann. Phys. (NY) **324**, 955 (2009).
- [48] S. Goedecker and C.J. Umrigar, Phys. Rev. A **55**, 1765 (1997).
- [49] D. Vogel, P. Krüger, and J. Pollmann, Phys. Rev. B **52**, R14316 (1995).
- [50] B. Baumeier, P. Krüger, and J. Pollmann, Phys. Rev. B **73**, 195205 (2006).
- [51] A. Filippetti and N. Spaldin, Phys. Rev. B **67**, 125109 (2003).
- [52] C. Toher, A. Filippetti, S. Sanvito, and K. Burke, Phys. Rev. Lett. **95**, 146402 (2005).
- [53] N. Gidopoulos, Phys. Rev. A **83**, 040502 (2011).
- [54] M.R. Pederson and B.M. Klein, Phys. Rev B **38**, 10319 (1988).
- [55] T. Baruah and M.R. Pederson, J. Chem. Theory and Comp. **5**, 834 (2009).
- [56] M. Head-Gordon and A. Dreuw, J. American Chem. Society. **126**, 4007 (2004).
- [57] A. Postnikov, J. Kortus, and M.R. Pederson, Phys. Stat. Solidi (b) **243**, 2533 (2006). See also: Psi-k Newsletter **61**, February 2004, 127 (2004).
- [58] A.A. Quong, M.R. Pederson, and J.L. Feldman, Sol. Stat. Comm. **87**, 535 (1993).

- [59] D. Porezag and M.R. Pederson, Phys. Rev B **54**, 7830 (1996).
- [60] P. Delugas, V. Fiorentini, and A. Filippetti, Phys. Rev B **71**, 134302 (2005).
- [61] J.G. Harrison, R.A. Heaton and C.C. Lin, J. Phys. B - Atomic, Molec. and Optical Phys. **16**, 2079 (1983).
- [62] A. Svane, V. Kanchana, G. Vaitheeswaran, G. Santi, W.M. Temmerman, Z. Szotek, P. Strange, and L. Petit, Phys. Rev. B **69**, 054427 (2004).
- [63] L. Petit, R. Tyer, Z. Szotek, W.M. Temmerman, and A. Svane, New J. Phys. **12**, 113041 (2011).
- [64] L. Petit, Z. Szotek, and W.M. Temmerman, Phys. Rev. B **76**, 115116 (2007); *ibid.* **80**, 045124 (2009); *ibid.* **81**, 045108 (2010).
- [65] M. Dauth, T. Körzdörfer, S. Kuemmel, J. Ziroff, N. Wiessner, A. Scholl, F. Reinert, M. Anita, and K. Shimada, Phys. Rev. Lett. **107**, 193002 (2011).
- [66] T. Körzdörfer, M. Mundt, and S. Kuemmel, Phys. Rev. Lett. **100**, 133004 (2008).
- [67] M. Lueders, A. Ernst, M. Daene, Z. Szotek, A. Svane, D. Koedderitzsch, W. Herbert, B.L. Gyorffy, and W.M. Temmerman, Phys. Rev. B **71**, 205109 (2005).
- [68] I.D. Hughes, M. Daene, A. Ernst, W. Hergert, M. Lueders, J. Poulter, J.B. Staunton, A. Svane, Z. Szotek, and W.M. Temmerman, Nature **446**, 650 (2007).
- [69] I.D. Hughes, M. Daene, A. Ernst, W. Hergert, M. Lueders, J.B. Staunton, Z. Szotek, and W.M. Temmerman, New J. Phys. **10**, 063010 (2008).
- [70] T. Baruah, J. Kortus, M.R. Pederson, R. Wesolowski, J.T. Haraldsen, J. Musfeldt, J.M. North, D. Zipse, and N.S. Dalal, Phys. Rev. B **70**, 214410 (2004).
- [71] J.G. Harrison, J. Chem. Phys. **78**, 4562 (1983).
- [72] V. Polo, J. Grafenstein, E. Kraka, and D. Cremer, Theor. Chem. Accounts **109**, 22 (2003).
- [73] J.L. Gazquez and E. Ortiz, Chem. Phys. Lett. **77**, 186 (1981).
- [74] S. Manoli and M.A. Whitehead, Phys. Rev. A **38**, 630 (1988).
- [75] Y. Zhang and W. Yang, Phys. Rev. Lett. **80**, 890 (1998).
- [76] O.A. Vydrov and G.E. Scuseria, J. Chem. Phys. **121**, 8187 (2004).
- [77] O.A. Vydrov and G.E. Scuseria, J. Chem. Phys. **122**, 184107 (2005).
- [78] O.A. Vydrov, G.E. Scuseria, J.P. Perdew, A. Ruzsinszky, and G.I. Csonka, J. Chem. Phys. **124**, 094108 (2006).
- [79] P. Mori-Sanchez, A.J. Cohen, and W. Yang, J. Chem. Phys. **125**, 201102 (2006).
- [80] S. Lany and A. Zunger, Phys. Rev. B **81**, 113201 (2010).

- [81] S. Lany and A. Zunger, Phys. Rev. B **78**, 235104 (2008).
- [82] K.A. Jackson and C.C. Lin, Phys. Rev B **38**, 12171 (1988).
- [83] D. Vieira and K. Capelle, J. Chem. Theory Comput. **6**, 3205 (2010).
- [84] G. H. Wannier, Phys. Rev. **52**, 191 (1937).
- [85] A. Svane and O. Gunnarsson, Phys. Rev. Lett. **65**, 1148 (1990).
- [86] Z. Szotek, W.M. Temmerman, and H. Winter, Phys. Rev. B **47**, 4029 (1993).
- [87] V.B. Oyeyemi, J. A. Keith, M. Pavone, and E.A. Carter, J. Chem. Phys. Lett. **3**, 289 (2012).
- [88] I. Dabo, A. Ferretti, N. Poilvert, Y.L. Li, N. Marzari, and M. Cococcioni, Phys. Rev. B **82**, 115121 (2010).
- [89] J.P. Perdew and M. Levy, Phys. Rev. Lett. **51**, 1884 (1983).
- [90] L.J. Sham and M. Schlüter, Phys. Rev. Lett. **51**, 1888(1983).
- [91] Z. Szotek, W.M. Temmerman, and H. Winter. Solid State Comm. **74**, 1031 (1990).
- [92] M.R. Pederson and C.C. Lin, Phys. Rev. B **35**, 2273 (1987).
- [93] S. Klüpfel, P. Klüpfel, and H. Jónsson, Phys, Rev. A **84**, 050501 (2011).
- [94] M. Levy, Phys. Rev. A **43**, 4637 (1991).
- [95] Y.H. Kim, I.H. Lee, S. Nagaraja, J.P. Leburton, R.Q. Hood, and R.M. Martin, Phys. Rev. B **61**, 5202 (2000).
- [96] S. Kurth, J. Mol. Struc. (Theochem) **501-502**, 189 (2000).
- [97] L. Pollack and J.P. Perdew, J. Phys.: Condens. Matter **12**, 1239 (2000).
- [98] R. Armiento and A.E. Mattsson, Phys. Rev. B **72**, 085108 (2005).
- [99] G.I. Csonka, O.A. Vydrov, G.E. Scuseria, A. Ruzsinszky, and J.P. Perdew, J. Chem. Phys. **126**, 244107 (2007).
- [100] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, X. Zhou, O.A. Vydrov, G.E. Scuseria, and K. Burke, Phys. Rev. Lett. **100**, 136406 (2008).
- [101] A.D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- [102] J.P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. **105**, 9982 (1996).
- [103] J. Heyd, G.E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003); *ibid.* **124**, 219906 (2006) (E).
- [104] L.E. Roy, T. Durakiewicz, R.L. Martin, J.E. Peralta, G.E. Scuseria, C.G. Olson, J.J. Joyce, and E. Guziewicz, J. Comput. Chem. **29**, 2288 (2008).