Unification of Perdew-Zunger Self-Interaction Correction, DFT+U, and Rung 3.5 Density Functionals

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Abstract

We unify the Perdew-Zunger self-interaction correction (PZSIC) to approximate density functional theory (DFT), the Hubbard correction DFT+U, and Rung 3.5 functionals within the Adiabatic Projection formalism. We modify the Kohn-Sham reference system, introducing electron self-interaction in selected states. Choosing those states as localized orbitals, localized atomic states, or states at each point in space recovers PZSIC, DFT+U, and Rung 3.5. Typical Hubbard U parameters approximate scaled-down PZSIC. A Rung 3.5 variant of DFT+U opens a band gap in the homogeneous electron gas.
Kohn-Sham density functional theory (DFT) is arguably the most widely-used electronic structure approximation across physics, chemistry, and materials science. DFT models a system of interacting electrons in external potential $v_{ext}(\vec{r})$, using a reference system of noninteracting Fermions corrected by a mean-field (Hartree) electron-electron repulsion and a formally exact exchange-correlation (XC) density functional. The ground-state energy $E$ becomes a unique and variational functional of the electron density $\rho$. Semilocal XC approximations give

$$E^{DFT}[\rho] = T_s[\rho] + \int d^3\vec{r} \rho(\vec{r})v_{ext}(\vec{r}) + U[\rho] + E_{XC}^{SL}[\rho, \rho].$$  \hspace{1cm} (1)\]

Self-interaction (delocalization) error is a major limitation of semilocal XC approximations. This error leads to incorrect nonzero electron-electron interaction energies for one-electron systems, and over-stabilization of open systems of fluctuating electron number.[1, 2] Self-interaction correction can improve predictions of band gaps, reaction barriers, excited states, electron affinities, and other properties. However, self-interaction error often mimics aspects of electron correlation, and correcting it can degrade predictions for lattice constants, bond energies, and strongly correlated systems.[3, 4] Strategies for addressing this paradoxical[4] zero-sum[5] tradeoff include the Perdew-Zunger self interaction correction (PZSIC),[6] Hubbard model DFT+U methods,[7–9] and Rung 3.5 functionals.[10]

The PZSIC ensures an approximate XC functional returns zero electron-electron interaction energy in any one-electron system:

$$E[\rho](PZSIC) = E^{DFT}[\rho] + \sum_{i=1}^{N} U[\rho_i] + E_{XC}^{SL}[\rho_i, 0].$$  \hspace{1cm} (2)\]

One-electron densities $\rho_{i\sigma} = |\phi_{i\sigma}|^2$, $\sigma = \alpha, \beta$ obey $\rho_{\sigma} = \sum_i \rho_{i\sigma}$. States $\phi_{i\sigma} = \sum_j L_{ij}^\sigma \psi_{j\sigma}$ are chosen as a localizing unitary transform $L^\sigma$ of the occupied spin-orbitals of the Kohn-Sham reference system $\psi_{i\sigma}$.\[11\] $U[\rho] = \frac{1}{2} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \rho(\vec{r}_1)\rho(\vec{r}_2)|\vec{r}_1 - \vec{r}_2|^{-1}$ denotes the Hartree electron repulsion of density $\rho$.

DFT+U adds a Hubbard-type model atop a DFT calculation, penalizing fractional (i.e., delocalized) occupancy of a set of predefined atomic states $\{\phi_m\}$. We consider the simplified rotationally invariant scheme:|8, 9|

$$E[\rho](DFT + U) = E^{DFT}[\rho] + \sum_{m=1}^{M} \frac{U_m}{2} \left(n_{ma} - n_{ma}^2\right).$$  \hspace{1cm} (3)\]
Here \( n_{m\sigma} = \sum_i |\langle \phi_m | \psi_i \rangle|^2 \) is the occupancy of the \( m \)th atomic state. (We assume throughout that atomic states are orthogonalized and occupation matrices are diagonal.) Hubbard parameter \( U_m \) controls the energetic penalty applied to state \( m \). Various schemes for determining \( U_m \) have been proposed.[9, 12]

Our Rung 3.5 functionals project the Kohn-Sham one-particle density matrix \( \gamma_\sigma(\vec{r}, \vec{r}') = \sum_i \psi_i(\vec{r}) \psi_i(\vec{r}') \) onto localized states \( \phi(\vec{r} - \vec{r}_g) \) centered at each point in space \( \vec{r}_g \), and use the projection as an ingredient in nonlocal approximate XC functionals:

\[
n_\sigma(\vec{r}_g) = \int d^3 \vec{r} \gamma_\sigma(\vec{r}_g, \vec{r}) \phi_{\text{RS5}}(\vec{r}_g - \vec{r}). \tag{4}
\]

Global, local, and range-separated hybrid functionals tune the tradeoffs of self-interaction by incorporating a fraction of localizing, one-electron-self-interaction-free exact exchange.[13]

Today, global and screened hybrid functionals are widely adopted and necessarily empirical,[13] DFT+U is widely adopted in solid-state physics,[14] local hybrids and PZSIC are experiencing renewed interest,[4] and Rung 3.5 functionals are under active development.[15] Formally, hybrid functionals can be derived through a generalized adiabatic connection,[16, 17] Rung 3.5 functionals introduce an upper bound within this derivation,[18] and the PZSIC and DFT+U are based on physical arguments and model Hamiltonians. DFT+U is connected to hybrid functionals and some correlated methods.[19–21] Additional formal connections between these approaches could drive new developments.

The present work presents a unified derivation of PZSIC, DFT+U, and Rung 3.5 methods, in terms of a reference system experiencing only electron self-interaction. The derivation uses the Adiabatic Projection formalism[22] employed in our generalization of PZSIC.[23] We begin with the general case. Let \( \{|\phi_{m\sigma}\}\} \) be a set of normalized \( \sigma \)-spin one-electron states. For each state, introduce a weight \( w_{m\sigma} \) and define a two-electron projection \( \hat{P}^2_{m\sigma} = |\phi_{m\sigma}\phi_{m\sigma}\rangle \langle \phi_{m\sigma}\phi_{m\sigma}| \) where \( \langle \vec{r}_1\vec{r}_2|\phi_{m\sigma}\phi_{m\sigma}\rangle = \phi_{m\sigma}(\vec{r}_1)\phi_{m\sigma}(\vec{r}_2) \). Consider a system of \( N = \sum_\sigma N_\sigma \) electrons in external potential \( v_{\text{ext}}(\vec{r}) \), with Hamiltonian \( \hat{H} = \hat{T} + \hat{V}_{\text{ee}} + \sum_{i=1}^N v_{\text{ext}}(r_i) \) and electron-electron interaction operator \( \hat{V}_{\text{ee}} = \frac{1}{2} \sum_{i,j=1}^N |\vec{r}_i - \vec{r}_j|^{-1} \). Define a projected electron-electron interaction operator and a generalized Hamiltonian

\[
\hat{V}_{\text{ee}}^P = \sum_{m\sigma} w_{m\sigma} \hat{P}^2_{m\sigma} \hat{V}_{\text{ee}} \hat{P}^2_{m\sigma}, \tag{5}
\]

\[
\hat{H}[\lambda, \mathbf{P}] = \hat{T} + \sum_{i=1}^N v_{\text{ext}}(\vec{r}_i) + \hat{V}_{\text{ee}}^P + \lambda \left( \hat{V}_{\text{ee}} - \hat{V}_{\text{ee}}^P \right). \tag{6}
\]
Here $\mathbf{P} = \{\phi_{m\sigma}, w_{m\sigma}\}$ denotes the states and weights, $\lambda = 0$ corresponds to the reference system, and $\lambda = 1$ corresponds to the real system. Define $\Psi[\lambda, \mathbf{P}, \rho]$ as the $N$-electron wavefunction that minimizes the expectation value of $\hat{H}[\lambda, \mathbf{P}]$ while returning density $\rho$. The Hohenberg-Kohn theorems ensure that there exists some unique and variational density functional which ensures that the reference system’s ground-state energy and density equal those of the real system,

$$U[\mathbf{P}, \rho] + E_{XC}[\mathbf{P}, \rho] = \int_0^1 d\lambda \langle \Psi[\lambda, \mathbf{P}, \rho] | \hat{V}_{ee} - \hat{V}_{ee}^P | \Psi[\lambda, \mathbf{P}, \rho] \rangle. \quad (7)$$

We assume the necessary N-representability conditions: for any $\lambda$, we assume that the ground-state density of the real system can be obtained from a pure ground state of $\hat{H}[\lambda, \mathbf{P}] + v_\lambda$ for some one-electron potential $v_\lambda$.

The reference system’s electron-electron interaction energy is zero, its ground-state wavefunction is a single Slater determinant, and the expectation value of $\hat{H}[\lambda = 0, \mathbf{P}]$ equals that of standard DFT. Consider $N$-electron Slater determinant $|\Phi\rangle$ formed from spin-orbitals $\{\psi_{i\sigma}\}$. The projection $\langle \phi_{m\sigma} | \phi_{m\sigma} \rangle |\Phi\rangle$ becomes $\sum_{i,j} (c_{rim\sigma}c_{jrn\sigma} - c_{jrn\sigma}c_{rim\sigma})$, where $c_{rim\sigma} = \langle \phi_{m\sigma} | \psi_{i\sigma} \rangle$. The expectation value of the $m$th term in Eq 5 becomes

$$\langle \Phi | \hat{P}_{ma}^2 \hat{V}_{ee} \hat{P}_{ma}^2 | \Phi \rangle = \sum_{i,j=1}^{N\sigma} c_{rim\sigma}^* c_{jrn\sigma} U[\rho_{ma}] (c_{rim\sigma}c_{jrn\sigma} - c_{jrn\sigma}c_{rim\sigma}), \quad (8)$$

$$= n_{ma}^2 U[\rho_{ma}] - n_{ma}^2 U[\rho_{ma}].$$

Here $n_{ma} = \sum_i |c_{ima\sigma}|^2$ is the occupancy of the $m$th projection state and $U[\rho_{ma}] = \langle \phi_{ma} | \phi_{ma} \rangle |\hat{V}_{ee} |\phi_{ma} \phi_{ma} \rangle$ is its Hartree self-repulsion. The self-Hartree and self-exchange terms cancel to ensure eq 8 is zero. The natural definition for the projected Hartree term in eq 7 is the difference between the Hartree energies of reference and real systems, $U[\mathbf{P}, \rho] = U[\rho] - \sum_{ma} w_{m\sigma} n_{ma}^2 U[\rho_{ma}]$. The ground-state energy of the real system becomes

$$E[\rho] = T_s[\rho] + \int d^3\vec{r} v_{ext}(\vec{r}) \rho(\vec{r}) + U[\rho] - \sum_{ma} w_{m\sigma} n_{ma}^2 U[\rho_{ma}] + E_{XC}[\mathbf{P}, \rho]. \quad (9)$$

Everything up to now is exact. To proceed, we choose the states and weights $\mathbf{P}$ and an approximation for the projected XC functional $E_{XC}[\mathbf{P}, \rho]$.

**PZSIC:** We choose $N_{\sigma}$ orthonormal localized projection states $|\phi_{ma}\rangle = \sum_i L_{mi}^\sigma |\psi_{i\sigma}\rangle$ matching the localized states in eq 2. This choice ensures that all $n_{ma} = 1$. We approximate $E_{XC}[\mathbf{P}, \rho]$ by combining states and weights $\mathbf{P}$ with an existing semilocal XC functional,

$$E_{XC}[\mathbf{P}, \rho]_{(PZSIC)} = E_{XC}^{SL}[\rho_\alpha, \rho_\beta] - \sum_{ma} w_{m\sigma} E_{XC}^{SL}[\rho_{ma}, 0]. \quad (10)$$
FIG. 1: DFT+U corrections (black thick line), PZSIC-LDA corrections (green), and PZSIC-PBE corrections (blue) for individual orbitals (eV), plotted as functions of orbital occupancy. (Left) 25% rescaled PZSIC for Ni (lines) and Ni$^{2+}$ (points) 3d orbitals, and $U=6$ eV. (Center) 25% rescaled PZSIC for Mn$^{4+}$ (lines) and Mn$^{2+}$ (points) 3d orbitals, and $U=4.67$ eV. (Right) Unscaled PZSIC for He (lines) and He$^+$ (points) 1s orbital, and $U = 16$ eV.

Choosing weights $w_{m\sigma} = 1$ and substituting eq 10 and $n_{m\sigma} = 1$ into eq 9 recovers the original PZSIC of eq 2. Choosing $w_{m\sigma} = 1/2$ recovers the scaled SIC of Klüpfel and coworkers.[24] Choosing $w_{m\sigma} = \int d^3\mathbf{r} (\tau_{W\sigma}(\mathbf{r})/\tau_{\sigma}(r))\rho_{m\sigma}(\mathbf{r})$ recovers the scaled SIC of Vydrov and Scuseria.[25] (Here $\tau_{\sigma}(\mathbf{r}) = \sum \|\nabla \psi_{i\sigma}(\mathbf{r})\|^2$ and $\tau_{W\sigma}(\mathbf{r}) = |\nabla \rho_{\sigma}(\mathbf{r})|/(4\rho_{\sigma}(\mathbf{r}))$.)

**DFT+U:** We choose projection states $|\phi_{m\sigma}\rangle$ as localized and orthogonalized atom-centered states. For example, in a calculation on solid nickel oxide NiO, we would choose five projection states of each spin per unit cell, corresponding to the five nickel 3d orbitals. We approximate $E_{XC}[P, \rho]$ following eq 10, noting that occupancies $n_{m\sigma}$ are no longer guaranteed to be 1. Substitution into eq 9 and rearrangement yields

$$E[\rho] = E^{DFT}[\rho] + \sum_{m\sigma} w_{m\sigma} U[\rho_{m\sigma}] \left( \frac{E^{SL}_{XC}[n_{m\sigma}\rho_{m\sigma}, 0]}{U[\rho_{m\sigma}]} - \frac{n_{m\sigma}^2}{2} \right)$$  \hspace{1cm} (11)

To recover eq 3, we further assume that the XC functional is linear in occupancy $n_{m\sigma}$ and perfectly cancels self-interaction at integer occupancy ($E^{SL}_{XC}[n_{m\sigma}\rho_{m\sigma}, 0] \approx n_{m\sigma} U[\rho_{m\sigma}]$), and define the Hubbard parameter as $U_m = 2w_{m\sigma} U[\rho_{m\sigma}]$.

With this derivation in hand, the magnitude of the Hubbard $U_m$ parameter for atomic state $|\phi_{m\sigma}\rangle$ depends on the state’s unscreened self-Coulomb interaction $U[\rho_{m\sigma}]$, weight $w_{m\sigma}$, and linearized semilocal approximate XC self-interaction. Our result is distinct from previous rationalizations of $U_m$, which invoke screening or renormalization to account for the effects of the other electrons in the system.[12, 20, 26] Figure 1 directly compares DFT+U to PZSIC, evaluated for fractional state occupancies using eq 11. PZSIC calculations use HF/def2-TZVP orbitals of isolated integer-charge high-spin atoms, computed with the
PySCF package.[27, 28] The $U_{\text{eff}} = 5 - 6 \text{ eV}$ employed in DFT+U simulations of nickel oxide[9, 29] approximately corresponds to a scaled-down PZSIC ($w_{m\sigma} = 1/4$) of the nickel 3d orbitals. Gratifyingly, this is consistent with the 1/4 scaling of exact exchange in the Heyd-Scuseria-Ernzerhof screened hybrid.[30] The $U_{\text{eff}} = 16 \text{ eV}$ used to correct fractional charge error of isolated helium atom[31] approximately corresponds to full PZSIC ($w_{m\sigma} = 1$) for the helium 1s orbital. DFT+U generally lies between the PZSIC computed with different choices of projection state[32] (e.g., neutral vs. cationic nickel) and XC functional (e.g. LDA[33] vs. PBE[34]).

**Rung 3.5:** We choose an infinite number of projection states $|\phi_\sigma(\vec{r}_m)\rangle$, one centered at each point in space $\vec{r}_m$. $\langle \vec{r} | \phi_\sigma(\vec{r}_m) \rangle = \phi_\sigma(\vec{r} - \vec{r}_m)$ denotes the state’s value at point $\vec{r}$. The sum over states $m$ in eq 9 becomes an integral over points $\vec{r}_m$, the weights $w_\sigma(\vec{r}_m)$ have units of (length)$^{-3}$, and $U[\rho_m]$ becomes $U[|\phi_\sigma(\vec{r} - \vec{r}_m)|^2]$, the Hartree self-repulsion of state $\phi_\sigma(\vec{r} - \vec{r}_m)$. The occupancies $n_{m\sigma}$ in eq 9 become Rung 3.5 projections similar to eq 4:

$$n_\sigma(\vec{r}_m) = \sum_i |\langle \psi_{i\sigma} | \phi_\sigma(\vec{r}_m) \rangle|^2,$$

$$= \int d^3\vec{r}_1 \int d^3\vec{r}_2 \gamma_\sigma(\vec{r}_1, \vec{r}_2) \phi_\sigma(\vec{r}_m - \vec{r}_1) \phi_\sigma(\vec{r}_m - \vec{r}_2).$$

Choosing the projection states to be Gaussians $\phi^G_\sigma(\vec{r} - \vec{r}_m) = (2\alpha/\pi)^{3/4} \exp(-\alpha|\vec{r} - \vec{r}_m|^2)$ recovers Rung 3.5 methods similar to those in Ref. 15. (Expanding the KS orbitals in $\{\chi_\mu(\vec{r} - \vec{R}_\mu)\}$, a set of Gaussian-type basis functions centered at points $\vec{R}_\mu$, gives analytically evaluable[35] $n_\sigma(\vec{r}_m) = \sum_{\mu\nu} A_{\mu}(\vec{r}_m) P_{\mu\nu} A_{\nu}(\vec{r}_m)$ where $A_{\mu}(\vec{r}_m) = \int d^3\vec{r} \chi_\mu(\vec{r} - \vec{R}_\mu) \phi^G(\vec{r} - \vec{r}_m)$ and $\gamma_{\sigma}(\vec{r}, \vec{r}') = \sum_{\mu\nu} \chi_{\mu}(\vec{r}) P^{\sigma}_{\mu\nu} \chi_{\nu}(\vec{r}')$.) Choosing instead a homogeneous electron gas (HEG) model for the projection states $\phi^L_\sigma(\vec{r} - \vec{r}_m) = \rho^{1/2}_\sigma(\vec{r}_m) \gamma^{LDA}(\rho_\sigma(\vec{r}_m), |\vec{r} - \vec{r}_m|)$ ensures that the occupancies $n_{\sigma}(\vec{r}_m)$ are independent of uniform density scaling. Here $4\pi^2 \gamma^{LDA}(\rho, u) = \sin(k_F u)/u^{3} - k_F \cos(k_F u)/u^2$ denotes the one-particle spin-density matrix of a HEG with Fermi vector $k_F = (6\pi^2 \rho_\sigma(\vec{r}_g))^{1/3}$.

At this point, one can make make many choices for the Rung 3.5 projected XC functional. Here we introduce a “DFT+R35U” approach based on eq 11,

$$E[\rho](DFT + R35U) = E^{DFT}[\rho] + \sum_\sigma \int d^3\vec{r}_m u(\vec{r}_m) \left( n_\sigma(\vec{r}_m) - n^2_\sigma(\vec{r}_m) \right).$$

The derivation of eq 13 parallels that of eq 11. Energy density $u(\vec{r}_m)$ is analogous to Hubbard energy $U_m$. This analogue of DFT+U contains no atom-centered states and no atom-dependent parameters.
FIG. 2: XC contribution to band energy $\epsilon(k)$ of the HEG. Exact exchange, LDA exchange, and LDA+R35U with Hubbard-like energy density $u = -0.1 \rho_\sigma v_{X\sigma}^{LDA}$.

We can apply eq 13 to the HEG, a system with $N_\sigma$ electrons in macroscopic volume $V$ giving translationally invariant density $\rho_\sigma(\vec{r}_m) = \rho_\sigma = N_\sigma / V$ and Kohn-Sham orbitals $\langle \vec{r} | \vec{k} \rangle = V^{-1/2} e^{i \vec{k} \cdot \vec{r}}$ occupied for $|\vec{k}| \leq k_F$. In contrast to eq 4, DFT+U cannot be applied to the HEG because there are no atomic states, and PZSIC applied to the HEG gives an incorrect total energy.[36] Choosing constant $u(\vec{r}_m) = u$ ensures translational invariance. Choosing projection states $\phi^L_\sigma(\vec{r} - \vec{r}_m)$ ensures that the projection onto KS orbitals $\langle \vec{k} | \phi^L_\sigma(\vec{r}_m) \rangle$ is $\rho_\sigma^{-1/2}$ for occupied states $|\vec{k}| < k_F$ and zero for unoccupied states. This ensures that all projection states are fully occupied ($n_\sigma(\vec{r}_m) = \int^{kF} d^3k |\langle \vec{k} | \phi^L_\sigma(\vec{r}_m) \rangle|^2 = 1$) and guarantees that eq 13 recovers $E^{DFT}[\rho]$. The nonlocal potential $\langle \vec{r}_1 | \hat{v}_{R35U} | \vec{r}_2 \rangle = \int d^3 \vec{r}_m u(\vec{r}_m)(1 - 2n_\sigma(\vec{r}_m))\phi^L_\sigma(\vec{r}_1 - \vec{r}_m)\phi^L_\sigma(\vec{r}_m - \vec{r}_2)$, defined from the functional derivative of eq 13 with respect to $\gamma_\sigma(\vec{r}_1, \vec{r}_2)$, gives band energy contribution $\langle \vec{k} | \hat{v}_{R35U} | \vec{k} \rangle$ equal to $-u \rho_\sigma^{-1}$ for occupied states and 0 for unoccupied states. Figure 2 illustrates the band energy contributions from exact exchange, LDA exchange, and LDA+R35U exchange choosing $u = -0.1 \rho_\sigma v_{X\sigma}^{LDA}$. The R35U correction shifts the occupied states and opens a bandgap without changing the total energy. Put another way, DFT+R35U provides an alternative derivation of a “scissor operator” applied to the HEG.[37]

We have generalized the PZSIC using projection onto active spaces, rather than individual orbitals, to introduce correlation into the reference system.[23] Here we briefly comment on similar generalizations of DFT+U and Rung 3.5 methods. For DFT+U, we can introduce interactions between the $\alpha$-spin and $\beta$-spin electrons in atomic state $\phi_m$ using $P^2_m = \sum_{\sigma, \sigma'} |\phi_m \sigma \phi_{m\sigma'}\rangle \langle \phi_m \sigma \phi_{m\sigma'}|$. The reference system now contains an opposite-spin in-
interaction $U[\rho_m]n_{\alpha_m}n_{\beta_m}$ alongside the self-interaction $U[\rho_m](n_{\alpha_m}^2 - n_{\alpha_m}^2)$. For Rung 3.5 methods, we introduce interactions between $\alpha$-spin and $\beta$-spin electrons in state $|\phi(\vec{r}_m)\rangle$ centered at $\vec{r}_m$. The reference system now contains an integral over the opposite-spin interactions $\int d^3\vec{r}_m u(\vec{r}_m)n_{\alpha}(\vec{r}_m)n_{\beta}(\vec{r}_m)$ alongside the self-interaction. In either case, the reference system’s electron-electron interaction energy is no longer zero, and its ground-state wavefunction is generally not a single Slater determinant. Approximating the reference wavefunction as a single Slater determinant yields analogues of the opposite-spin terms in DFT+U+J and “judiciously modified DFT” generalizations,[38, 39] and the opposite-spin Rung 3.5 correlation in M11plus,[15] which is based on Becke’s real-space nondynamical correlation model.[40]

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