Projected Hybrid Density Functionals: Method and Application to Core Electron Ionization

Benjamin G. Janesko

Department of Chemistry & Biochemistry, Texas Christian University, Fort Worth, TX 76129, USA

(*Electronic mail: b.janesko@tcu.edu)

(Dated: 14 October 2022)

This work presents a new class of hybrid density functional theory (DFT) approximations, incorporating nonlocal exact exchange in predefined states such as core atomic orbitals (AOs). These projected hybrid density functionals are a flexible generalization of range-separated hybrids. This work derives projected hybrids using the Adiabatic Projection formalism. One projects the electron-electron interaction operator onto the chosen predefined states, reintroduces the projected operator into the noninteracting Kohn-Sham reference system, and introduces a density functional approximation for the remaining electron-electron interactions. Projected hybrids are readily implemented existing density functional codes, requiring only a projection of the one-electron density matrices and exchange operators entering existing routines. This work also presents a first application: a core-projected Perdew-Burke-Ernzerhof hybrid PBE0c70, in which the fraction of nonlocal exact exchange is increased from 25% to 70% in core AOs. Automatic selection of the projected AOs provides a black-box model chemistry appropriate for both core and valence electron properties. PBE0c70 predicts core orbital energies that accurately recover core-electron binding energies of second- and third-row elements, without degrading PBE0’s good performance for valence-electron properties.
Projected Hybrids

I. INTRODUCTION

Kohn-Sham density functional theory (DFT) is the most widely-used electronic structure approximation across chemistry, physics, and materials science.\textsuperscript{1} DFT models a system of interacting electrons in terms of a reference system of noninteracting Fermions, corrected by a mean-field (Hartree) electron repulsion and an exchange-correlation (XC) density functional incorporating all many-body effects.\textsuperscript{2} Standard approximations to the XC functional can capture important aspects of covalent bonding, at the expense of delocalization and self-interaction errors that lead to overbinding and over-delocalization.\textsuperscript{3,4} Hybrid XC approximations mitigate these effects by including a fraction of nonlocal exact exchange, effectively reintroducing part of the electron-electron interaction into the reference system.\textsuperscript{5} However, introducing a fixed fraction of the entire electron-electron interaction leads to pervasive and resilient zero-sum tradeoffs between under-binding and over-delocalization.\textsuperscript{2,6,7}

The generalized range-separated adiabatic connection provides a way to optimize these tradeoffs.\textsuperscript{5,8–15} This approach separates the electron-electron interaction operator $\hat{V}_{ee}$ into short-range and long-range pieces, for example

$$\hat{V}_{ee} = \sum_{i>j} \frac{1}{r_{ij}} = \sum_{i>j} \frac{\text{erf}(\mu r_{ij})}{r_{ij}} + \frac{\text{erfc}(\mu r_{ij})}{r_{ij}},$$

$$= \hat{V}_{ee}^{LR} + \hat{V}_{ee}^{SR}. \tag{1}$$

Part of the interaction, typically the long-range part, is reintroduced into the noninteracting reference system. The Hohenberg-Kohn theorems ensure that the real system’s ground-state energy and density can be obtained from an exact wavefunction calculation on the long-range-interacting reference system, corrected by a density functional for the remaining short-range Hartree-exchange-correlation energy. By relying on approximate XC functionals for only part of the electron-electron interaction, these approaches can provide beyond-zero-sum accuracy for certain properties, without the expense of a correlated wavefunction calculation on the real system.\textsuperscript{15} Several groups have explored different approximations for the long-range-interacting reference system wavefunction, including coupled-cluster theory,\textsuperscript{16} multireference approaches,\textsuperscript{13,17} the density matrix renormalization group,\textsuperscript{18} and the random phase approximation.\textsuperscript{19}

Range-separated hybrids are an especially widely adopted approach.\textsuperscript{20} These methods approximate the reference system wavefunction as a single Slater determinant, corrected by a density functional for full-range correlation.\textsuperscript{5} The development of range-separated exchange functionals\textsuperscript{21,22}
Projected Hybrids

has enabled broad adoption of range-separated hybrids. Long-range-corrected (LC) hybrids introduce the long-range interaction into the reference system, and are widely adopted for Rydberg and charge-transfer excited states, noncovalent interactions, and more.\textsuperscript{23–25} Screened hybrids introduce the short-range interaction into the reference system, and are widely adopted for semiconductors, metal oxides, and core excitations.\textsuperscript{26,27} However, introducing a fixed range separation $\mu$ and fixed fraction of the short- and long-range interactions leaves remaining zero-sum tradeoffs.\textsuperscript{7} Recent efforts to treat these tradeoffs include system-dependent range separation,\textsuperscript{28,29} local range separation,\textsuperscript{30} range separations parameterized to particular properties,\textsuperscript{31} and other approximations reviewed in ref 2.

A. Adiabatic Projection

The Adiabatic Projection approach generalizes the range-separated adiabatic connection.\textsuperscript{32} One replaces the range-separate interaction of eq 1 with a projected interaction defined by a set of two-electron projection operators \( \{ \hat{P}_m^{(2)} \} \):

\[
\hat{V}_{Pee} = \sum_m c_m \sum_{i>j} \hat{P}_m^{(2)}(i,j) \frac{1}{r_{ij}} \hat{P}_m^{(2)}(i,j).
\]  

(The notation \( \hat{P}_m^{(2)}(i,j) \) means that the operator acts on electrons \( i \) and \( j \).) One then reintroduces the projected interaction into the reference system. Just as for the range-separated adiabatic connection, the Hohenberg-Kohn theorems ensure that the real system’s exact ground-state energy and density can be obtained from an exact wavefunction calculation on the projected-interacting reference system, corrected by a formally exact density functional for the projected Hartree-exchange-correlation energy.

We have applied the Adiabatic Projection approach to several contemporary problems in DFT. Projecting onto one-electron states \( \hat{P}_m^{(2)} = |\phi_m\phi_m\rangle \langle \phi_m\phi_m| \), \( \langle \vec{r}|\phi_m\rangle = \phi_m(\vec{r}) \) introduces only self-interaction into the reference system. Choosing those one-electron states as localized Kohn-Sham spin-orbitals, and approximating the projected XC functional in terms of the orbital densities, recovers the Perdew-Zunger self-interaction correction (PZSIC).\textsuperscript{33,34} Other choices of one-electron states provides connections between the PZSIC, the Hubbard model DFT+U, and Rung 3.5 approximations.\textsuperscript{35} Projecting onto active spaces of multiple occupied and virtual orbitals, and treating the reference system with a complete active-space self-consistent field (CASSCF) wavefunction, generalizes the PZSIC into a wavefunction-in-DFT approach.\textsuperscript{34}
Projected Hybrids

B. Projected hybrids

This work introduces projected hybrid density functionals inspired by range-separated hybrids. One projects the electron-electron interaction onto predefined states such as core atomic orbitals (AOs), approximates the reference system wavefunction as a single Slater determinant, and combines a projected exchange functional with a full-range correlation functional. This flexible approach permits exact exchange admixture in chemically appropriate regions, requires minimal modification to existing codes, and (unlike active-space approaches) can be incorporated into “black-box” model chemistries.

C. DFT for core electron properties

This pilot study introduces a core-projected hybrid functional targeted to simulate core- and valence-electron properties. Core-electron spectroscopies probe the chemical environment of nuclei and give element-specific information on bonding and oxidation state. The growing availability of bright X-ray sources has led to increasing interest in core electron spectroscopies. DFT and time-dependent (TD-)DFT simulations are widely adopted to interpret core electron spectra. DFT orbital energies, generated from accurate Kohn-Sham or generalized Kohn-Sham potentials, can accurately predict the vertical ionization potentials (IPs) of both core and valence electrons. (In this approach, the first ionization potential is modeled as the negative of the highest occupied molecular orbital energy \( \text{IP} = -\epsilon_{\text{HOMO}} \), and core ionization potentials are modeled as the negative of core molecular orbital energies.) Accurate XC potentials and orbital energies are also important for linear response TD-DFT simulations of X-ray absorption spectra.

Self-interaction error significantly impacts DFT-predicted core electron properties. For second-row elements Li-Ne, the core orbital energies predicted by standard global hybrid functionals differ by tens of eV from experimental K-edge core IPs. Comparable errors occur for TD-DFT predictions of core excitation energies. Self-interaction errors are even worse for the more compact cores of third-row elements Na-Ar. Increasing the admixture of nonlocal exact exchange can improve predicted core IPs at the expense of a “zero-sum” degradation in valence electron properties. Delta-self-consistent-field (\( \Delta \text{SCF} \)) approaches explicitly compute non-Aufbau core-ionized or core-excited state wavefunctions, providing a reduced impact of self-interaction error and a widely adopted practical solution. However, \( \Delta \text{SCF} \) approaches can suffer from difficul-
Projected Hybrids

ties converging the non-Aufbau states, require one SCF calculation for each nucleus of interest in a large molecule, do not readily yield transition moments or vibronic couplings, and may still be significantly impacted by self-interaction error in heavier elements.\textsuperscript{47} The state-of-the-art for modeling X-ray fluorescence combines linear response TD-DFT with a constant shift taken from ΔSCF calculations.\textsuperscript{48} Mitigating the impact of self-interaction error on core elections, without degrading the treatment of valence electrons, could broaden the impact of inexpensive TD-DFT approaches.\textsuperscript{46}

There has been significant interest in using self-interaction correction or exact exchange admixture to improve TD-DFT predictions of core electron spectroscopies. Tu and coworkers predicted core ionization potentials by applying a rescaled PZSIC to B3LYP-computed orbital energies.\textsuperscript{44} Several workers have developed range-separated hybrids that incorporate a large fraction of short-range nonlocal exchange. Hirao and coworkers modified their LCgau-BOP hybrid to include additional short-range nonlocal exchange, and reported improved TD-DFT core excitations for second-row atoms.\textsuperscript{50,51} Besley and coworkers reparameterized screened hybrid functionals to improve TD-DFT predictions of core excitations. They required different parameterizations for second-row and third-row atoms,\textsuperscript{31} which may be another manifestation of the zero-sum tradeoffs discussed above. Chai and coworkers introduced short- and long-range correction (SLC) hybrids including 100% nonlocal exchange at short and long range. SLC core orbital energies accurately predicted core ionization energies of second-row atoms, and TD-DFT with SLC functionals accurately predicted a range of core, valence, and charge-transfer excitations.\textsuperscript{52} Kaupp and coworkers showed that local hybrid functionals, incorporating a position-dependent admixture of exact exchange, provided balanced accuracy for TD-DFT predictions of the core excitations of second-row elements, along with valence, charge-transfer and Rydberg excitations.\textsuperscript{46} Nakata and coworkers introduced an orbital-dependent hybrid incorporating different fractions of HF exchange in different Kohn-Sham orbitals. The authors reported TD-DFT calculations using the coupling operator technique of Roothaan, and found accurate core-excitation energies for second-row atoms.\textsuperscript{45} This work was extended to a core-valence-Rydberg approach,\textsuperscript{53} and is related to other orbital-dependent DFT methods.\textsuperscript{54}
Projected Hybrids

D. Core projected hybrids

This pilot study presents projected hybrids that incorporate additional nonlocal exchange in core AOs. Enhancing the Perdew-Burke-Ernzherhof global hybrid PBE0\textsuperscript{55–57} with 70% exact exchange in core AOs yields core molecular orbital (MO) energies that accurately predict second- and third-row K-edge ionization potentials, without a zero-sum degradation in valence electron properties. Numerical results are comparable to the core-valence hybrid of Nakata and coworkers,\textsuperscript{45} without requiring the cumbersome coupling operator technique. The rest of this work presents a derivation of projected hybrids, details of the core-projected hybrid tested here, and numerical results.

II. DERIVATION

This derivation of projected hybrid density functionals is based on published derivations of range-separated hybrids.\textsuperscript{5} In Kohn-Sham DFT, the exact ground-state energy of an N-electron system is expressed in terms of a noninteracting reference system and a density functional correction:

\[ E = \min_{\Phi} \left( \langle \Phi | \hat{T} + \hat{V}_{\text{ext}} | \Phi \rangle + E_{\text{HXC}}[\rho_\Phi] \right). \]  

Here \( \hat{T} \) and \( \hat{V}_{\text{ext}} \) are operators for the kinetic energy and external potential experienced by the reference system. \( E_{\text{HXC}}[\rho] \) is the universal Hartree-exchange-correlation (HXC) density functional. Given the exact HXC functional, the reference system’s minimizing single-determinant wavefunction \( \Phi \) yields ground-state energy \( E \) and electron density \( \rho_\Phi \) equal to the exact values.

Range-separated and projected hybrids respectively introduce the range-separated (eq 1) and projected (eq 2) interactions into the reference system. The present work introduces a new choice of the projection in eq 2, based on an orthonormal set of \( N_P \) single-particle states \( \{\phi_{m}^{(P)}\} \) that are independent of the Kohn-Sham orbitals:

\[ \hat{P}^{(2)} = \sum_{m,n}^{N_P} |\phi_{m}^{(P)}\langle \phi_{n}^{(P)}| \phi_{m}^{(P)}\phi_{n}^{(P)} \rangle |. \]  

(For example, core-projected hybrids will choose \( \{\phi_{m}^{(P)}\} \) by orthogonalizing the core AOs.) The ground-state energy is expressed as

\[ E = \min_{\psi_{LR}} \left( \langle \psi_{LR}^{L} | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee}^{LR} | \psi_{LR}^{L} \rangle + E_{\text{HXC}}^{SR}[\rho_{\psi_{LR}^{L}}] \right), \]  

(5)
Projected Hybrids

in the generalized range-separated adiabatic connection and as

$$E = \min_{\Psi^P} \left( \langle \Psi^P | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee}^P | \Psi^P \rangle + E_{\text{HXC}}^P [\rho^P \Psi] \right), \quad (6)$$

in the present work. Minimizing wavefunctions $\Psi^{LR}$ and $\Psi^P$ are generally multideterminant. Eq 5-6 yield the exact density and energy of the real system given the exact short-range and projected HXC functionals, respectively. The short-range HXC functional depends on the chosen range separation ($\mu$ in eq 1), and the projected HXC functional depends on the projection $\hat{P}^{(2)}$ and thus on the chosen $\{ \phi_n^{(P)} \}$.

Range-separated and projected hybrids are derived by restricting the minimizing wavefunctions in eq 5-6 to be single determinant:

$$E^{(0)}_{\text{RSH}} = \min_{\Phi^{LR}} \left( \langle \Phi^{LR} | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee}^{LR} | \Phi^{LR} \rangle + E_{\text{HXC}}^{SR} [\rho^{LR}] \right), \quad (7)$$

$$E^{(0)}_{\text{PH}} = \min_{\Phi^P} \left( \langle \Phi^P | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee}^P | \Phi^P \rangle + E_{\text{HXC}}^P [\rho^P \Phi] \right). \quad (8)$$

The minimizing determinants are given by the Euler-Lagrange equations:

$$\left( \hat{T} + \hat{V}_{\text{ext}} + \hat{j} - (\hat{K}^{SR} + \hat{V}_{XC}^{SR}) \right) | \Phi^{LR} \rangle = \epsilon_{LR} | \Phi^{LR} \rangle, \quad (9)$$

$$\left( \hat{T} + \hat{V}_{\text{ext}} + \hat{j} - (\hat{K}^P + \hat{V}_{XC}^P) \right) | \Phi^P \rangle = \epsilon_P | \Phi^P \rangle. \quad (10)$$

Here $\hat{j}$ is the Hartree potential, the sum of long-range and short-range terms (eq 9) or projected and unprojected terms (eq 10). $\hat{K}, \hat{K}_{SR}, \hat{K}_P$ are the full-range, short-range, and projected nonlocal exchange operators. $\epsilon_{LR}$ and $\epsilon_P$ are Lagrange multipliers for the normalization constraint.

The restriction to single determinants means that eq 7-8 do not yield the exact energy and density, even with the exact short-range or projected Hartree-exchange-correlation functionals. Nevertheless, they can be used as a reference to express the exact energy as $E = E_{\text{RSH}} + E_{\text{C}}^{LR}$ or $E_{\text{PH}} + E_{\text{C}}^P$. Conventional LC hybrids use a standard (full-range) correlation functional to model the sum of correlation in the long-range-interacting reference system $E_{\text{C}}^{LR}$, and the correlation piece of $E_{\text{HXC}}^{SR}$. This work uses a standard (unprojected) correlation functional to model the sum of correlation in the projected-interacting reference system, and the correlation piece of $E_{\text{HXC}}^P$. The hybrid functionals’ the total energies are

$$E_{\text{RSH}} = \min_{\Phi^{LR}} \left( \langle \Phi^{LR} | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee}^{LR} | \Phi^{LR} \rangle + U_{\text{SR}} [\rho^{LR} \Phi] + E_{\text{HXC}}^{SR} [\rho^{LR}] + E_{\text{C}}^{SL} [\rho^{LR}] \right), \quad (11)$$

for range-separated hybrids and

$$E_{\text{PH}}^{(0)} = \min_{\Phi^P} \left( \langle \Phi^P | \hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{ee}^P | \Phi^P \rangle + U_P [\rho^P \Phi] + E_{\text{HXC}}^{SL} [\rho^P] + E_{\text{C}}^{SL} [\rho^P] \right), \quad (12)$$
Projected Hybrids

for projected hybrids.

Practical implementation of range-separated hybrid functionals requires explicit construction of range-separated semilocal exchange functionals $E_{XS}^{SL}[\rho]$, based on models for the exchange hole. This is not the case for projected exchange functionals, where one may pass projected one-particle density matrices to unmodified semilocal exchange functionals. Ref 34 provides a detailed derivation of this approach, as a generalization of the Perdew-Zunger self-interaction correction.

III. IMPLEMENTATION

This section presents the working equations for a projected hybrid’s generalized Kohn-Sham energy and potential. We consider the case of a core-projected hybrid calculation in an atomic orbital (AO) basis. The reference system’s single-determinant $N$-electron wavefunction $|\Phi^P\rangle$ is made up of orthonormal one-electron spin-orbitals (MOs) $\{|\psi_{i\sigma}\rangle\}$, each of which is expanded in a nonorthogonal basis set of $N_{basis}$ real AOs $\{|\chi_{\mu}\rangle\}$. The overlap $\langle \chi_{\mu} | \chi_{\nu} \rangle = S_{\mu\nu}$, where $S_{\mu\nu}$ is a matrix element of the $N_{basis} \times N_{basis}$ overlap matrix $S$. The MOs are expanded as $|\psi_{i\sigma}\rangle = \sum_{\mu} c_{i\sigma\mu} |\chi_{\mu}\rangle$. The core-projected hybrid has $N_{core} \ll N_{basis}$ AOs assigned as core AOs. The orthonormal projection states in eq 4 are denoted core states $\{|\phi_{m}^{(c)}\rangle\}$, and are obtained by orthogonalizing the core AOs. Orthogonalization requires $\left(S^{(c)}\right)^{-1}_{\mu\nu}$, the matrix inverse of the $N_{core} \times N_{core}$ matrix of core AO overlaps.

Proceeding requires a one-electron projection operator $\hat{P}$ onto the orthogonalized core AOs. This operator’s representation in the full AO basis is

$$\hat{P} = \sum_{\mu\nu} |\chi_{\mu}\rangle P_{\mu\nu} \langle \chi_{\nu}|.$$  

(13)

Matrix element $P_{\mu\nu}$ of $N_{basis} \times N_{basis}$ matrix $P$ equals $\left(S^{(c)}\right)^{-1}_{\mu\nu}$ when both $\chi_{\mu}$ and $\chi_{\nu}$ are core AOs, and equals zero elsewhere. This matrix obeys $\text{PSP} = P$. The two-electron operator in eq 2 becomes $\hat{P}^{(2)}(i,j) = \hat{P}(i)\hat{P}(j)$, where $\hat{P}(i)$ denotes the projection of eq 13 acting on electron $i$. For any one-electron operator $\sum_{i} \hat{A}(i)$, the expectation value of the projected operator $\sum_{i} \hat{P}(i)\hat{A}(i)\hat{P}(i)$ becomes

$$\langle \Phi | \sum_{i} \hat{P}(i)\hat{A}(i)\hat{P}(i) | \Phi \rangle = \sum_{i\sigma} \langle \psi_{i\sigma} | \sum_{\mu\mu'} |\chi_{\mu}\rangle P_{\mu\mu'} \langle \chi_{\mu'}| \hat{A} \left( \sum_{\nu\nu'} |\chi_{\nu}\rangle P_{\nu\nu'} \langle \chi_{\nu'}| \right) |\psi_{i\sigma}\rangle ;$$  

(14)

$$= \sum_{i\sigma} \sum_{\mu\nu} c_{i\sigma\mu}^{*} A_{\mu\nu}^{P} c_{i\sigma\nu}.$$
Projected Hybrids

This equation introduces matrix elements of the projected one-electron operator, which are defined as

\[ A_{\mu\nu}^P = \sum_{\mu',\nu'\nu''} S_{\mu\mu'} P_{\mu'\nu'\nu''} A_{\mu''\nu''} P_{\nu''\nu} S_{\nu'\nu}. \]  

(15)

\( A_{\mu\nu} = \langle \chi_\mu | \hat{A} | \chi_\nu \rangle \) denotes matrix elements of the unprojected operator. The expectation value of the projected two-electron integral operator \( \hat{V}_{ee}^P = \sum_{i \geq j} \hat{P}(i)\hat{P}(j)\hat{V}_{ee}(i,j)\hat{P}(i)\hat{P}(j) \) is

\[
\langle \Phi | \hat{V}_{ee}^P | \Phi \rangle = \frac{1}{2} \sum_{i} \sum_{j} \langle \psi_i | \psi_j \rangle \left( \sum_{\mu\nu\nu'} \langle \chi_\mu | \chi_{\nu'} \rangle P_{\mu\nu} P_{\nu'\nu} \langle \chi_{\nu'} | \chi_\nu \rangle \right) \hat{V}_{ee} \\
\times \left( \sum_{\lambda\eta'\lambda'\eta} \langle \chi_\mu | \chi_{\nu'} \rangle P_{\lambda\lambda'} P_{\eta'\eta} \langle \chi_{\nu'} | \chi_\nu \rangle \left( \langle \psi_i | \psi_j \rangle - \langle \psi_j | \psi_i \rangle \right) \right),
\]

\[
= \frac{1}{2} \sum_{i} \sum_{j} c_{i\sigma\mu}^* c_{j\sigma'\nu}^* \langle \mu\nu | \lambda\eta \rangle^P (c_{i\sigma\lambda} c_{j\sigma'\eta} - c_{j\sigma'\lambda} c_{i\sigma\eta}).
\]

The projected two-electron integrals are defined analogous to eq 15:

\[
\langle \mu\nu | \lambda\eta \rangle^P = \sum_{\mu'\nu'\nu''\lambda'\eta'\eta''} S_{\mu\mu'} P_{\mu'\nu'\nu''} P_{\nu''\nu} \langle \mu''\nu'' | \lambda''\eta'' \rangle P_{\lambda''\lambda} S_{\lambda\lambda'} P_{\eta''\eta} \langle \lambda'\eta' | \lambda\eta \rangle^P \]

(17)

In practice, implementing projected hybrids does not require explicitly evaluating these projected AO-basis two-electron integrals. One only requires one-electron projections of density matrices and exchange operators. (However, the projected AO-basis two-electron integrals may be required for multi-determinant treatments of the projected interacting reference system, discussed in sec VI.) As shown in eq 10, the Hartree piece of eq 16 is combined with the remainder of the Hartree interaction from the projected Hartree-exchange-correlation density functional, yielding the usual \( J \) matrix. The exchange piece of eq 16 can be written as

\[
E_X^P = -\frac{1}{2} \sum_{i} \sum_{j} c_{i\sigma\mu}^* c_{j\sigma'\nu}^* \langle \mu\nu | \lambda\eta \rangle^P c_{j\sigma\lambda} c_{i\sigma\eta},
\]

(18)

\[
= -\frac{1}{2} \sum_{i} \sum_{\mu\eta} c_{i\sigma\mu}^* K_{\mu\eta}^P [\gamma_{\sigma\eta}^P] c_{i\sigma\eta}.
\]

Here \( K_{\mu\eta}^P [\gamma_{\sigma\eta}^P] \) denotes the projected (as in eq 15) nonlocal exact exchange operator constructed from projected density matrix \( \gamma_{\sigma\eta}^P \). Matrix elements of the the conventional AO-basis \( \sigma \)-spin one-particle density matrix are

\[
\gamma_{\sigma\nu\lambda} = \sum_{i} c_{i\sigma\nu}^* c_{i\sigma\lambda}.
\]  

(19)
Projected Hybrids

The projected density matrix is defined as

$$\gamma_{\sigma \nu \lambda}^P = \sum_{\nu' \lambda' \nu'' \lambda''} P_{\nu \nu'} S_{\nu' \nu''} \gamma_{\sigma \nu'' \lambda''} S_{\lambda'' \lambda'} P_{\lambda' \lambda}. \quad (20)$$

(Note that the projected density matrix eq 20 is $PS\gamma SP$, whereas the projected one-electron operator eq 15 is $SPAPS$.) The unprojected exchange operator is constructed from the projected density matrix and unprojected AO-basis two-electron integrals as,

$$K_{\mu \eta}[\gamma^P] = \sum_{\nu'' \lambda''} \langle \mu \nu'' | \lambda'' \eta \rangle \gamma_{\sigma \nu'' \lambda''}^P. \quad (21)$$

Projecting this operator as in eq 15 recovers the first line of eq 18.

The final step in the implementation involves the projected exchange functional, the analogue of the range-separated exchange functionals used in range-separated hybrids. As suggested above, we obtain the projected exchange functional by passing the projected density matrix to existing semilocal exchange functionals. We consider a standard $\sigma$-spin semilocal exchange functional

$$E_{X}^{SL}[\gamma_{\sigma}] = \int d^3r \ e_{X}^{SL}[\rho_{\sigma}(\bar{r}), |\nabla \rho_{\sigma}(\bar{r})| \ldots], \quad (22)$$

$$\rho_{\sigma}(\bar{r}) = \sum_{\mu \nu} \chi_{\mu}(\bar{r}) \gamma_{\mu \nu \sigma} \chi_{\nu}(\bar{r}). \quad (23)$$

We define the projected exchange functional as the difference between $E_{X}^{SL}$ evaluated with projected vs. unprojected density matrices. The total energy of a projected hybrid functional thus becomes

$$E = \sum_{ij} \sum_{\mu \nu} c_{i \sigma}^* \left( h_{\mu \nu} + \frac{1}{2} J_{\mu \nu} - \frac{1}{2} K_{\mu \nu}^{P}[\gamma^P_{\sigma}] \right) + E_{X}^{SL}[\gamma_{\sigma}] - \sum_{\sigma} E_{X}^{SL}[\gamma_{\sigma}^P] \quad (24)$$

Here $h_{\mu \nu}$ is a matrix element of the kinetic and external potential operators, $J_{\mu \nu}$ is a matrix element of the standard full-range Hartree potential, $E_{X}^{SL}[\gamma_{\sigma}]$ is a standard semilocal exchange-correlation functional evaluated on the full density matrix, and $E_{X}^{SL}[\gamma_{\sigma}^P]$ is the exchange piece of the semilocal functional (eq 22) evaluated on the projected density matrix of eq 20. The Fock-like matrix defined by $\partial E/\partial c_{i \mu \sigma} = \sum_{\nu} F_{\mu \nu \sigma} c_{i \nu \sigma}$, becomes (compare with eq 10)

$$F_{\mu \nu \sigma} = h_{\mu \nu} + J_{\mu \nu} + \left( V_{X}^{SL}[\gamma_{\sigma}] \right)_{\mu \nu \sigma} - K_{\mu \nu}^{P}[\gamma_{\sigma}^P] - \left( V_{X}^{SLP}[\gamma_{\sigma}^P] \right)_{\mu \nu} \quad (25)$$

Here the unprojected semilocal exchange operator is constructed from the projected density matrix in the usual way

$$\left( V_{X}^{SL}[\gamma_{\sigma}^P] \right)_{\mu \nu} = \int d^3r \chi_{\mu}(\bar{r}) \frac{\delta e_{X}^{SL}}{\delta P_{\sigma}(\bar{r})} \chi_{\nu}(\bar{r}) + \ldots \quad (26)$$
Projected Hybrids

Projecting this operator as in eq 15 recovers the \( (V_{\text{SLP}}^\gamma \gamma_{\sigma}^P \gamma_{\alpha}^P)_{\mu\nu} \) in eq 25. Operationally, one constructs the projected AO-basis density matrix \( \text{PS} \gamma\text{SP} \), passes this to standard routines for constructing \( \text{K} \) and the semilocal exchange potential, then projects the operators (e.g. \( \text{SPKPS} \)) before use. Because the projection states are independent of the MOs, self-consistent implementation merely requires these projections of one-particle density matrices and exchange operators.

IV. METHODS

This work uses an implementation of eq 24-25 into the PySCF electronic structure package. The implementation is freely available online at github.com/bjanesko. Just as range-separated hybrids can include different fractions of short- and long-range exact exchange, the present implementation includes different fractions of projected exact exchange \( \alpha_c \) and global exact exchange \( \alpha_0 \). This work adopts the notation "FcX", where "F" is a standard XC functional and "X" is the fraction of nonlocal exchange in core AOs. X="HF" is equivalent to X=100. For example, PBEcHF combines semilocal PBE with 100% HF exchange in AOs. Most benchmark calculations treat the PBE0c70 functional, combining PBE0 with 70% nonlocal exchange in core AOs (\( \alpha_0 = 25\% \), \( \alpha_c = 70\% \)).

In this pilot study, total energies and Fock-like matrices (eq 25) are computed from Hartree-Fock one-particle density matrices. Generalized Kohn-Sham orbital energies are obtained from a single diagonalization of the Fock-like matrices constructed from Hartree-Fock density matrices. Most calculations use the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation, the PBE0 global hybrid incorporating 25% nonlocal exchange,\(^{56,57}\) the PBEHH global hybrid incorporating 50% nonlocal exchange, or the HFPBE combination of nonlocal exchange and PBE correlation. Test calculations treat the BLYP,\(^{59,60}\) the three-parameter global hybrid B3LYP,\(^{61,62}\) the Tao-Perdew-Staroverov-Scuseria (TPSS) and Strongly Constrained and Appropriately Normed (SCAN) meta-GGAs,\(^{63,64}\) and the SCAN0 global hybrid. Other test calculations use the Gaussian 16 package,\(^{65}\) and also include the M06L, M06, M06-2X, and M06-HF global hybrids,\(^{66–68}\) the HSE06, N12SX, and MN12XS screened hybrids,\(^{26,69}\) and the LC-\( \omega \)PBE, \( \omega \)B97X-D, M11, Lc-BLYP, and CAM-B3LYP long-range-corrected hybrids.\(^{70–72}\) These calculations use post-HF total energies and self-consistent orbital energies. For the systems tested here, the two approaches methods are nearly identical: single-shot PBE with PySCF predicts CH\(_3\)Cl valence and core IP 7.14 and 2738.9 eV, self-consistent PBE with Gaussian 16
Projected Hybrids

predicts valence and core IP 7.09 and 2739.7 eV. Calculations use several AO basis sets, including
the 6-311++G(2d,2p) Pople-type basis set,\(^{73,74}\) the cc-pVnZ correlation-consistent basis sets,\(^{75}\)
the cc-pCVTZ and cc-pCVQZ basis sets designed for core electron properties, and the def2-SVP,
def2-TZVP, def2-QZVP basis sets.\(^{76}\) All molecular geometries are B3LYP/6-311++G(2d,2p) op-
timized.

This black-box study includes an automated choice of core AOs. Each second- and third-row
element is assigned a cutoff kinetic energy as 1.4 times the kinetic energy from the most diffuse
uncontracted core orbital in the STO-2G basis set. All s-type contrated AOs with kinetic energy
above that cutoff are assigned to the core. For example, the STO-2G basis set for lithium atom
includes a contracted 1s AO with exponents 6.16 and 1.10 au. The most diffuse exponent gives
a kinetic energy \((3/2)1.10\) au and a cutoff \((1.4)(3/2)1.10\) au=2.3 au. All s-type contracted AOs
centered on a Li atom \(\{\chi_{Li}^\mu\}\), whose kinetic energy expectation value \(\langle \chi_{Li}^\mu | \frac{1}{2} \nabla^2 | \chi_{Li}^\mu \rangle\) is above that
threshold, are assigned as core. For the 6-311++G(2d,2p) basis set, this approach gives one core
AOs for each second-row element and three core AOs for each third-row element.

V. RESULTS

A. Validation

Table I illustrates the overall performance of this approach, as well as the basis set dependence.
The table shows valence, Cl core, and C core ionization potentials of CH\(_3\)Cl, computed from
the corresponding generalized Kohn-Sham orbital energies. Calculations compare the PBEcHF
core-projected hybrid (100% nonlocal exchange in core AOs) with PBE (no nonlocal exchange)
and HFPBE (100% nonlocal exchange globally). As expected, the core-projected hybrid recovers
the PBE valence IP to within 0.01 eV, and recovers the HFPBE core IP to within a few percent.
Results are robust across basis sets, even as the number of core AOs changes from 2 to 11. This
confirms that the projected hybrids and the core AO selection process perform as expected.

Table II illustrates core-projected hybrid calculations using a variety of standard XC function-
als. All core-projected hybrids use 100% nonlocal exchange in cores. For HFPBE, the unprojected
and core-projected functionals are identical by construction. Otherwise, core projection increases
the predicted core IP of second- and third-row atoms, without much affecting the HOMO energies.
Whereas the unprojected functionals’ predicted core IP range over 30 eV for C and 110 eV for Cl,
Projected Hybrids

TABLE I. Valence, C core, and Cl core ionization potentials of methylene chloride CH$_2$Cl (eV), computed as the negative of GKS orbital energies, evaluated in various basis sets.

| Basis        | $N_{\text{core}}$ | Valence | C atom core | Cl atom core |
|--------------|-------------------|---------|-------------|--------------|
|              |                   | PBE     | PBEcHF      | HFPBE        | PBE         | PBEcHF      | HFPBE        |
| STO-3G       | 2                 | 4.94    | 4.94        | 11.64        | 267.3       | 303.5       | 303.7        | 2709.0   | 2814.1       | 2822.1       |
| 3-21G        | 2                 | 7.09    | 7.09        | 13.15        | 270.5       | 307.2       | 306.9        | 2719.0   | 2826.7       | 2833.2       |
| 6-31G(d)     | 2                 | 7.04    | 7.04        | 13.09        | 271.8       | 307.8       | 308.2        | 2738.4   | 2844.3       | 2852.7       |
| 6-311++G(2d,2p) | 4             | 7.14    | 7.14        | 13.17        | 272.0       | 311.3       | 308.4        | 2738.9   | 2847.7       | 2853.2       |
| cc-pvdz      | 4                 | 6.95    | 6.95        | 13.03        | 272.0       | 307.7       | 308.4        | 2738.7   | 2847.6       | 2853.0       |
| cc-pvtz      | 3                 | 7.05    | 7.05        | 13.09        | 271.8       | 308.5       | 308.2        | 2738.8   | 2847.6       | 2853.1       |
| cc-pcvtz     | 5                 | 7.06    | 7.06        | 13.09        | 271.8       | 307.8       | 308.2        | 2738.8   | 2847.9       | 2853.1       |
| cc-pvqz      | 5                 | 7.09    | 7.09        | 13.11        | 271.8       | 308.5       | 308.2        | 2738.9   | 2847.8       | 2853.2       |
| cc-pcvqz     | 11                | 7.09    | 7.09        | 13.11        | 271.8       | 307.8       | 308.2        | 2738.9   | 2847.3       | 2853.2       |
| def2-svp     | 2                 | 6.79    | 6.79        | 12.93        | 272.0       | 308.0       | 308.3        | 2737.5   | 2843.8       | 2851.8       |
| def2-tzvp    | 3                 | 7.06    | 7.06        | 13.08        | 271.8       | 299.9       | 308.2        | 2738.8   | 2848.2       | 2853.1       |
| def2-qzvp    | 6                 | 7.10    | 7.10        | 13.12        | 271.8       | 303.7       | 308.2        | 2738.9   | 2848.5       | 2853.2       |

TABLE II. Valence, C core, and Cl core ionization potentials of methylene chloride (eV), computed as the negative of GKS orbital energies, unmodified XC functional F vs. core-projected functional FcHF, 6-311++G(2d,2p) basis set.

| Functional F | Valence | C atom core | Cl atom core |
|--------------|---------|-------------|--------------|
|              | F       | FcHF        | F            | FcHF         | F            | FcHF         |
| PBE          | 7.14    | 7.14        | 272.0        | 311.3        | 2738.9       | 2847.7       |
| PBE0         | 8.64    | 8.64        | 281.1        | 310.6        | 2767.4       | 2849.0       |
| PBEHH        | 10.15   | 10.15       | 290.2        | 309.8        | 2796.0       | 2850.4       |
| HFPBE        | 13.17   | 13.17       | 308.4        | 308.4        | 2853.2       | 2853.2       |
| BLYP         | 6.96    | 6.96        | 272.7        | 311.6        | 2740.7       | 2848.6       |
| B3LYP        | 8.17    | 8.17        | 279.7        | 311.3        | 2762.4       | 2849.9       |
| TPSS         | 7.33    | 7.33        | 274.8        | 310.7        | 2747.9       | 2848.6       |
| SCAN         | 7.55    | 7.55        | 275.9        | 310.3        | 2753.6       | 2850.3       |
| SCAN0        | 8.89    | 8.89        | 284.0        | 309.7        | 2778.4       | 2851.0       |

the core-projected functionals’ core IP are all within 6 eV of each other.
Projected Hybrids

FIG. 1. Computed atomization energy (abscissa) and Cl core IP (ordinate) of formyl chloride HCOCl. "X" denotes standard DFT functionals. Straight line denotes global hybrids of PBE including between 0 and 70% exact exchange. "Ref" is accurate reference values.

B. Benchmarks

Figure 1 highlights the “zero-sum” trade-offs between predictions of valence and core properties, focusing on the atomization energy and core IP of formyl chloride HCOCl. Calculations use the def2-TZVP basis set. The figure shows the atomization energy on the abscissa, and the Cl core IP (negative of computed Cl 1s orbital energy) on the ordinate. Reference values are the 2820.6 eV core IP from ref 47, and a new CBS-QB3\textsuperscript{77} computed atomization energy 355.9 kcal/mol. Calculations compare core-projected PBE0c70 to a broad range of density functionals: semilocal PBE, BLYP, TPSS, M06L; global hybrid PBE0, PBEHandH, BHandH, M06-2X, M06-HF, and SOGGA11-X; and range-separated hybrids M11, ωB97X-D, HSE06, LC-ωPBE, LC-BLYP, CAM-B3LYP, N12-SX, MN12-SX. The straight line is results for PBE global hybrids including between 0 and 70% exact exchange.

The PBE global hybrid results clearly highlights the zero-sum tradeoff between valence and core properties. Introducing a fixed fraction of the entire nonlocal exchange interaction increases
Projected Hybrids

the predicted core IP, but also makes the predicted atomization energy less positive. PBE0 is near-optimal for the atomization energy, but underbinds the core electron. PBE70 is near-optimal for the core electron, but underestimates the chemical bond strengths. Most global hybrids lie close to this “zero-sum” line, accurately reproducing the atomization energy while underestimating the core IP. Long-range corrected hybrids tend to further underestimate the core IP. Screened hybrids MN12SX and N12SX, and the highly parameterized SOGGA11X, M06-2X, and M06-HF better approach the reference value. For this system, the core-projected hybrid PBE0c70 clearly provides the best agreement with the reference values employed.

The rest of this work presents a more detailed assessment of PBE0c70 on two data sets of core-electron ionization potentials. The first set is 33 K-shell ionization potentials of second-row atoms, from 14 small molecules, referenced to experiment.\(^4\) (In this dataset, “MBO” denotes 2-mercaptobenzoxazole.) The second set is 15 K-shell ionization potentials of third-row atoms, from 15 small molecules, referenced to nonrelativistic \(\Delta MP2\) calculations.\(^4\). Calculations use the 6-311++G(2d,2p) basis set and B3LYP/6-311++G(2d,2p) geometries.

Table III reports a validation of the valence properties predicted by core-projected PBE0c70. As the goal is to recover the underlying PBE0 global hybrid, mean absolute deviations MAD are referenced to PBE0. Gratifyingly, PBE0c70 gives ionization potentials within 0.01 eV of PBE0, and atomization energies within 1 kcal/mol of PBE0. Much larger deviations in valence properties are seen for the PBE70 global hybrid.

Tables IV-V report second- and third-row core ionization potentials for the benchmark data sets. As in previous work, PBE0 core orbital energies are not an accurate predictor for core ionization potentials, giving MAD > 10 eV for second-row atoms and > 40 eV for third-row atoms. PBE70 significantly improves the core IP. Gratifyingly, PBE0c70 is nearly as accurate as PBE70, while maintaining PBE0 performance for valence electron properties.

**VI. DISCUSSION**

These results motivate further exploration of projected hybrids. Core-projected hybrids appear to be a promising choice for beyond-zero-sum TD-DFT simulations of X-ray absorbance and fluorescence of second- and third-row atoms, including vibronic structure, without the need for \(\Delta SCF\) corrections.\(^4\) Other projections, for example projections onto metal \(d\)-electron states within a single unit cell, could provide connections between screened hybrid and DFT+U simulations of
### TABLE III. Valence ionization potentials IP (eV) and atomization energies AE (kcal/mol), referenced to PBE0.

| Molecule   | IP\(\text{PBE0}\) | IP\(\text{PBE0c70}\) | IP\(\text{PBE70}\) | AE\(\text{PBE0}\) | AE\(\text{PBE0c70}\) | AE\(\text{PBE70}\) |
|------------|--------------------|-----------------------|--------------------|-------------------|----------------------|-------------------|
| CO         | 11.21              | 11.21                 | 14.21              | 251.6             | 251.4                | 231.4             |
| H\(_2\)O   | 8.93               | 8.93                  | 12.64              | 224.9             | 224.9                | 213.9             |
| CH\(_4\)   | 11.13              | 11.13                 | 14.01              | 413.6             | 413.3                | 412.4             |
| CH\(_3\)CN | 9.75               | 9.75                  | 12.23              | 294.7             | 294.0                | 268.9             |
| CH\(_3\)COOH | 8.16              | 8.16                  | 11.53              | 792.1             | 791.4                | 761.6             |
| Glycine    | 7.64               | 7.64                  | 10.59              | 956.1             | 955.3                | 915.6             |
| MBO        | 6.71               | 6.71                  | 8.54               | 1734.5            | 1731.8               | 1666.5            |
| Ph\(_\text{CH3}\) | 7.26               | 7.26                  | 8.97               | 1666.1            | 1663.8               | 1632.9            |
| Ph\(_\text{NH2}\) | 6.24               | 6.24                  | 8.1                | 1542.7            | 1540.5               | 1500.8            |
| Ph\(_\text{OH}\) | 6.83               | 6.83                  | 8.72               | 1472.2            | 1470.1               | 1429.0            |
| Ph\(_\text{F}\) | 7.57               | 7.57                  | 9.42               | 1380.4            | 1378.4               | 1339.8            |
| C\(_2\)H\(_2\) | 8.73               | 8.73                  | 10.96              | 399.7             | 399.0                | 384.7             |
| C\(_2\)H\(_4\) | 8.17               | 8.17                  | 10.2               | 557.6             | 557.0                | 548.7             |
| C\(_2\)H\(_6\) | 9.74               | 9.74                  | 12.49              | 704.8             | 704.1                | 701.8             |
| Al\(_\text{H3}\) | 8.61               | 8.61                  | 11                 | 197.0             | 196.2                | 203.4             |
| Al\(_\text{H2Cl}\) | 8.75               | 8.75                  | 11.24              | 217.8             | 216.9                | 221.9             |
| Al\(_\text{H2F}\) | 8.89               | 8.89                  | 11.43              | 259.4             | 258.5                | 257.7             |
| Si\(_4\)   | 9.99               | 9.99                  | 12.49              | 300.5             | 299.8                | 307.6             |
| H\(_3\)Si\(_\text{OH}\) | 8.62               | 8.62                  | 11.58              | 422.5             | 421.7                | 419.6             |
| H\(_3\)Si\(_\text{Cl}\) | 9.12               | 9.12                  | 11.75              | 298.3             | 297.5                | 302.8             |
| Ph\(_3\)   | 8.02               | 8.03                  | 10.19              | 222.2             | 221.8                | 221.3             |
| H\(_3\)PO   | 7.8                | 7.8                   | 10.95              | 295.0             | 294.4                | 283.0             |
| H\(_2\)POO\(_\text{OH}\) | 8.06               | 8.06                  | 11.22              | 410.7             | 410.0                | 388.7             |
| CH\(_3\)SH | 7.1                | 7.1                   | 9.45               | 456.7             | 456.2                | 451.5             |
| H\(_2\)CS   | 6.95               | 6.95                  | 9.28               | 308.5             | 308.0                | 296.4             |
| H\(_2\)S    | 7.8                | 7.8                   | 10.17              | 169.0             | 168.8                | 166.5             |
| CH\(_3\)Cl | 8.64               | 8.64                  | 11.36              | 385.1             | 384.7                | 380.7             |
| HCO\(_\text{Cl}\) | 9.28               | 9.28                  | 12.25              | 354.6             | 354.2                | 330.5             |
| HCl        | 9.69               | 9.69                  | 12.45              | 99.5              | 99.4                 | 97.7              |
| MAD        | —                  | 0.00                  | 2.55               | —                 | 0.87                 | 17.07             |
TABLE IV. Core ionization potentials for second-row atoms (eV).

| Molecule | Atom | Reference | PBE0  | PBE0c70 | PBE70  |
|----------|------|-----------|-------|---------|--------|
| CO       | O    | 542.1     | 525.9 | 549.6   | 548.4  |
|          | C    | 295.5     | 282.7 | 300.4   | 299.1  |
| H₂O      | O    | 539.9     | 523.2 | 546.9   | 545.6  |
| CH₄      | C    | 290.8     | 278.5 | 296.2   | 294.9  |
| CH₃CN    | N    | 405.6     | 392.2 | 413.0   | 411.7  |
|          | CH₃  | 292.4     | 280.5 | 298.1   | 296.1  |
| CH₃COOH  | COOH | 540.1     | 524.5 | 548.2   | 546.9  |
|          | COOH | 538.4     | 522.8 | 546.5   | 545.2  |
|          | COOH | 295.4     | 283.6 | 301.3   | 300.0  |
|          | CH₃  | 291.6     | 279.7 | 297.3   | 296.1  |
| Glycine  | COOH | 540.2     | 524.6 | 548.4   | 547.1  |
|          | COOH | 538.4     | 522.9 | 546.7   | 545.4  |
|          | N    | 405.4     | 391.9 | 412.6   | 411.2  |
|          | COOH | 295.3     | 283.6 | 301.3   | 300.0  |
|          | CH   | 295.2     | 280.6 | 298.3   | 297.0  |
| MBO      | O    | 540.6     | 525.6 | 549.3   | 548.0  |
|          | N    | 407.0     | 394.5 | 415.2   | 413.9  |
|          | CS   | 295.7     | 284.5 | 302.2   | 300.9  |
|          | CO   | 293.9     | 281.8 | 299.5   | 298.2  |
|          | CCN  | 293.0     | 281.5 | 299.2   | 297.9  |
|          | CCO  | 297.9     | 306.7 | 280.3   | 297.3  |
| C₆H₅CH₃ | CH₃  | 290.9     | 279.5 | 297.2   | 295.9  |
|          | CCH₃ | 290.1     | 279.3 | 296.9   | 295.7  |
| C₆H₅NH₂ | N    | 405.3     | 392.2 | 412.9   | 411.5  |
|          | CN   | 291.2     | 280.5 | 298.2   | 296.9  |
| C₆H₅OH  | O    | 538.9     | 523.9 | 547.6   | 546.3  |
|          | CO   | 292.0     | 281.3 | 298.9   | 297.6  |
| C₆H₅F   | F    | 693.3     | 674.3 | 701.0   | 699.8  |
|          | CF   | 292.9     | 281.9 | 299.6   | 298.3  |
| C₂H₂     | C    | 291.2     | 279.5 | 297.2   | 295.9  |
| C₂H₄     | C    | 290.7     | 279.2 | 296.9   | 295.6  |
| C₂H₆     | C    | 290.6     | 278.7 | 296.4   | 295.1  |
| MAE      |      | ——        | 13.0  | 7.0     | 5.3    |
TABLE V. Core ionization potentials for third-row atoms (eV).

| Molecule        | Reference | PBE0  | PBE0c70 | PBE70  |
|-----------------|-----------|-------|---------|--------|
| AlH₃            | 1565.1    | 1528.5| 1565.4  | 1566.8 |
| AlH₂Cl          | 1565.8    | 1530.0| 1567.0  | 1568.3 |
| AlH₂F           | 1566.0    | 1529.4| 1566.4  | 1567.7 |
| SiH₄            | 1843.2    | 1803.3| 1843.2  | 1844.9 |
| H₅SiOH          | 1844.0    | 1804.2| 1844.1  | 1845.7 |
| H₅SiCl          | 1844.3    | 1805.1| 1845.1  | 1846.7 |
| PH₃             | 2145.8    | 2101.7| 2144.6  | 2146.5 |
| H₃PO            | 2148.3    | 2104.7| 2147.7  | 2149.6 |
| H₂POOH          | 2149.1    | 2105.7| 2148.7  | 2150.6 |
| CH₃SH           | 2471.0    | 2422.8| 2468.8  | 2471.0 |
| H₂CS            | 2471.2    | 2422.9| 2468.9  | 2471.0 |
| H₂S             | 2471.7    | 2423.2| 2469.2  | 2471.4 |
| CH₃Cl           | 2820.3    | 2767.4| 2816.4  | 2818.9 |
| HCOCl           | 2820.6    | 2768.4| 2817.4  | 2819.8 |
| HCl             | 2821.4    | 2768.2| 2817.1  | 2819.6 |
| MAE             | —         | 44.1  | 1.6     | 1.3    |

periodic systems. Going beyond the single-determinant approximation in eq 12 could provide an interesting alternative to active space selection and orbital localization in multiconfigurational methods. Consider for example a calculation on a large organometallic complex known to possess multireference character in the metal $d$ electrons. Rather than choosing an active space of correlated MOs, one could project the metal atom $d$ AOs into the reference system, leaving only $\sim 10^3$ nonzero AO-basis two-electron integrals. Algorithms that account for this extreme sparsity of AO-basis integrals could potentially provide near-full-CI accuracy for the entire reference system, giving a “black-box” alternative to multireference wavefunction-in-DFT approaches. Overall, the present results motivate further development of Adiabatic Projection hybrids, just as Refs 26 and 23 motivated broad adoption of screened and LC hybrids.

VII. ACKNOWLEDGMENTS

The author acknowledges the Texas Advanced Computing Center at the University of Texas at Austin for providing HPC resources that have contributed to the research results reported within this paper.
Projected Hybrids

REFERENCES

1. P. Verma and D. G. Truhlar, Status and challenges of density functional theory, Trends in Chemistry 2, 302 (2020).

2. B. G. Janesko, Replacing hybrid density functional theory: motivation and recent advances, Chem. Soc. Rev. (2021).

3. P. Mori-Sánchez, A. J. Cohen, and W. Yang, Localization and delocalization errors in density functional theory and implications for band-gap prediction, Phys. Rev. Lett. 100, 146401 (2008).

4. J. P. Perdew et al., Understanding band gaps of solids in generalized kohn–sham theory, Proc. Natl. Acad. Sci. 114, 2801 (2017).

5. J. Toulouse, I. C. Gerber, G. Jansen, A. Savin, and J. G. Ángyán, Adiabatic-connection fluctuation-dissipation density-functional theory based on range separation, Phys. Rev. Lett. 102, 096404 (2009).

6. A. Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria, Spurious fractional charge on dissociated atoms: Pervasive and resilient self-interaction error of common density functionals, J. Chem. Phys. 125, 194112 (2006).

7. B. G. Janesko, E. Proynov, J. Kong, G. Scalmani, and M. J. Frisch, Practical density functionals beyond the overdelocalization–underbinding zero-sum game, The Journal of Physical Chemistry Letters 8, 4314 (2017).

8. A. Savin, A combined density functional and configuration interaction method, Int. J. Quantum Chem. 34, 59 (1988).

9. A. Savin and H.-J. Flad, Density functionals for the yukawa electron-electron interaction, Int. J. Quantum Chem. 56, 327 (1995).

10. T. Leininger, H. Stoll, H.-J. Werner, and A. Savin, Combining long-range configuration interaction with short-range density functionals, Chem. Phys. Lett. 275, 151 (1997).

11. W. Yang, Generalized adiabatic connection in density functional theory, J. Chem. Phys. 109, 10107 (1998).

12. J. Toulouse, F. Colonna, and A. Savin, Long-range–short-range separation of the electron-electron interaction in density-functional theory, Phys. Rev. A 70, 062505 (2004).

13. E. Fromager, J. Toulouse, and H. J. A. Jensen, On the universality of the long-/short-range separation in multiconfigurational density-functional theory, J. Chem. Phys. 126, 074111 (2007).
Projected Hybrids

14 A. Savin, Models and corrections: Range separation for electronic interaction—lessons from density functional theory, J. Chem. Phys. 153, 160901 (2020).

15 K. Pernal and M. Hapka, Range-separated multiconfigurational density functional theory methods, WIREs Computational Molecular Science 12 (2021).

16 E. Goll, H.-J. Werner, and H. Stoll, A short-range gradient-corrected density functional in long-range coupled-cluster calculations for rare gas dimers, Physical Chemistry Chemical Physics 7, 3917 (2005).

17 E. Fromager, R. Cimiraglia, and H. J. A. Jensen, Merging multireference perturbation and density-functional theories by means of range separation: Potential curves for be$_2$, mg$_2$, and ca$_2$, Physical Review A 81, 024502 (2010).

18 E. D. Hedegaard, S. Knecht, J. S. Kielberg, H. J. A. Jensen, and M. Reiher, Density matrix renormalization group with efficient dynamical electron correlation through range separation, J. Chem. Phys. 142, 224108 (2015).

19 B. G. Janesko, T. M. Henderson, and G. E. Scuseria, Long-range-corrected hybrids including random phase approximation correlation, J. Chem. Phys. 130, 081105 (2009).

20 T. M. Henderson, B. G. Janesko, and G. E. Scuseria, Range separation and local hybridization in density functional theory, The Journal of Physical Chemistry A 112, 12530 (2008).

21 H. Iikura, T. Tsuneda, T. Yanai, and K. Hirao, A long-range correction scheme for generalized-gradient-approximation exchange functionals, J. Chem. Phys. 115, 3540 (2001).

22 M. Ernzerhof and J. P. Perdew, Generalized gradient approximation to the angle- and system-averaged exchange hole, J. Chem. Phys. 109, 3313 (1998).

23 A. Dreuw, J. L. Weisman, and M. Head-Gordon, Long-range charge-transfer excited states in time-dependent density functional theory require non-local exchange, J. Chem. Phys. 119, 2943 (2003).

24 E. D. Hedegaard, F. Heiden, S. Knecht, E. Fromager, and H. J. A. Jensen, Assessment of charge-transfer excitations with time-dependent, range-separated density functional theory based on long-range MP2 and multiconfigurational self-consistent field wave functions, The Journal of Chemical Physics 139, 184308 (2013).

25 M. A. Rohrdanz, K. M. Martins, and J. M. Herbert, A long-range-corrected density functional that performs well for both ground-state properties and time-dependent density functional theory excitation energies, including charge-transfer excited states, J. Chem. Phys. 130, 054112 (2009).
Projected Hybrids

26 J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118, 8207 (2003).

27 Y. Wang et al., M06-sx screened-exchange density functional for chemistry and solid-state physics, Proc. Natl. Acad. Sci. 117, 2294 (2020).

28 T. Stein, L. Kronik, and R. Baer, Reliable prediction of charge transfer excitations in molecular complexes using time-dependent density functional theory, J. Am. Chem. Soc. 131, 2818 (2009).

29 T. Körzdörfer and J.-L. Brédas, Organic electronic materials: Recent advances in the DFT description of the ground and excited states using tuned range-separated hybrid functionals, Acc. Chem. Res. 47, 3284 (2014).

30 A. V. Krukau, G. E. Scuseria, J. P. Perdew, and A. Savin, Hybrid functionals with local range separation, J. Chem. Phys. 129, 124103 (2008).

31 N. A. Besley, M. J. G. Peach, and D. J. Tozer, Time-dependent density functional theory calculations of near-edge x-ray absorption fine structure with short-range corrected functionals, Physical Chemistry Chemical Physics 11, 10350 (2009).

32 B. G. Janesko and E. N. Brothers, Virtual experiments on real asphaltenes: Predicting properties using quantum chemical simulations of structures from non-contact atomic force microscopy, Energy & Fuels (2022).

33 J. P. Perdew and A. Zunger, Self-interaction correction to density-functional approximations for many-electron systems, Phys. Rev. B 23, 5048 (1981).

34 B. G. Janesko, Adiabatic projection: Bridging ab initio, density functional, semiempirical, and embedding approximations, J. Chem. Phys. 156, 014111 (2022).

35 B. G. Janesko, Systematically improvable generalization of self-interaction corrected density functional theory, The Journal of Physical Chemistry Letters 13, 5698 (2022).

36 P. Norman and A. Dreuw, Simulating x-ray spectroscopies and calculating core-excited states of molecules, Chemical Reviews 118, 7208 (2018).

37 N. A. Besley, Density functional theory based methods for the calculation of x-ray spectroscopy, Accounts of Chemical Research 53, 1306 (2020).

38 A. Seidl, A. Görling, P. Vogl, J. A. Majewski, and M. Levy, Generalized Kohn-Sham schemes and the band-gap problem, Phys. Rev. B 53, 3764 (1996).

39 D. P. Chong, O. V. Gritsenko, and E. J. Baerends, Interpretation of the kohn–sham orbital energies as approximate vertical ionization potentials, The Journal of Chemical Physics 116, 1760 (2002).
Projected Hybrids

40. N. P. Bellafont, P. S. Bagus, and F. Illas, Prediction of core level binding energies in density functional theory: Rigorous definition of initial and final state contributions and implications on the physical meaning of kohn-sham energies, The Journal of Chemical Physics 142, 214102 (2015).

41. P. Verma and R. J. Bartlett, Increasing the applicability of density functional theory. III. do consistent kohn-sham density functional methods exist?, The Journal of Chemical Physics 137, 134102 (2012).

42. Y. Zhang, J. D. Biggs, D. Healion, N. Govind, and S. Mukamel, Core and valence excitations in resonant x-ray spectroscopy using restricted excitation window time-dependent density functional theory, The Journal of Chemical Physics 137, 194306 (2012).

43. P. Verma and R. J. Bartlett, Increasing the applicability of density functional theory. v. x-ray absorption spectra with ionization potential corrected exchange and correlation potentials, The Journal of Chemical Physics 145, 034108 (2016).

44. G. Tu, V. Carravetta, O. Vahtras, and H. Ågren, Core ionization potentials from self-interaction corrected kohn-sham orbital energies, J. Chem. Phys. 127, 174110 (2007).

45. A. Nakata, Y. Imamura, T. Otsuka, and H. Nakai, Time-dependent density functional theory calculations for core-excited states: Assessment of standard exchange-correlation functionals and development of a novel hybrid functional, The Journal of Chemical Physics 124, 094105 (2006).

46. T. M. Maier, H. Bahmann, A. V. Arbuznikov, and M. Kaupp, Validation of local hybrid functionals for TDDFT calculations of electronic excitation energies, J. Chem. Phys. 144, 074106 (2016).

47. N. A. Besley, Density functional theory calculations of core–electron binding energies at the k-edge of heavier elements, Journal of Chemical Theory and Computation 17, 3644 (2021).

48. A. A. E. Fouda and N. A. Besley, Improving the predictive quality of time-dependent density functional theory calculations of the x-ray emission spectroscopy of organic molecules, Journal of Computational Chemistry 41, 1081 (2020).

49. N. A. Besley, A. T. B. Gilbert, and P. M. W. Gill, Self-consistent-field calculations of core excited states, The Journal of Chemical Physics 130, 124308 (2009).

50. J.-W. Song, S. Tokura, T. Sato, M. A. Watson, and K. Hirao, An improved long-range corrected hybrid exchange-correlation functional including a short-range gaussian attenuation (LCgau-BOP), The Journal of Chemical Physics 127, 154109 (2007).
51 J.-W. Song, M. A. Watson, A. Nakata, and K. Hirao, Core-excitation energy calculations with a long-range corrected hybrid exchange-correlation functional including a short-range gaussian attenuation (LCgau-BOP), J. Chem. Phys. 129, 184113 (2008).
52 C.-W. Wang, K. Hui, and J.-D. Chai, Short- and long-range corrected hybrid density functionals with the d3 dispersion corrections, J. Chem. Phys. 145, 204101 (2016).
53 A. Nakata, Y. Imamura, and H. Nakai, Hybrid exchange-correlation functional for core, valence, and rydberg excitations: Core-valence-rydberg b3lyp, The Journal of Chemical Physics 125, 064109 (2006).
54 D. S. Ranasinghe, M. J. Frisch, and G. A. Petersson, A density functional for core-valence correlation energy, The Journal of Chemical Physics 143, 214111 (2015).
55 J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77, 3865 (1996).
56 C. Adamo and V. Barone, Toward reliable density functional methods without adjustable parameters: The PBE0 model, J. Chem. Phys. 110, 6158 (1999).
57 G. E. Scuseria and P. Y. Ayala, Linear scaling coupled cluster and perturbation theories in the atomic orbital basis, J. Chem. Phys. 111, 8330 (1999).
58 Q. Sun et al., Recent developments in the PySCF program package, J. Chem. Phys. 153, 024109 (2020).
59 C. Lee, W. Yang, and R. G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37, 785 (1988).
60 A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. A 38, 3098 (1988).
61 A. D. Becke, Density-functional thermochemistry. III. the role of exact exchange, J. Chem. Phys. 98, 5648 (1993).
62 J. R. Cheeseman, G. W. Trucks, T. A. Keith, and M. J. Frisch, A comparison of models for calculating nuclear magnetic resonance shielding tensors, J. Chem. Phys. 104, 5497 (1996).
63 J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Climbing the density functional ladder: Nonempirical meta–generalized gradient approximation designed for molecules and solids, Phys. Rev. Lett. 91, 146401 (2003).
64 J. Sun, A. Ruzsinszky, and J. P. Perdew, Strongly constrained and appropriately normed semilocal density functional, Phys. Rev. Lett. 115, 036402 (2015).
Project Hybrids

65 Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lippari, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

66 Y. Zhao and D. G. Truhlar, A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions, J. Chem. Phys. 125, 194101 (2006).

67 Y. Zhao and D. G. Truhlar, Density functionals for noncovalent interaction energies of biological importance, J. Chem. Theory Comput. 3, 289 (2006).

68 Y. Zhao and D. G. Truhlar, Density functional for spectroscopy: No long-range self-interaction error, good performance for rydberg and charge-transfer states, and better performance on average than b3lyp for ground states, J. Phys. Chem. A 110, 13126 (2006).

69 R. Peverati and D. G. Truhlar, Screened-exchange density functionals with broad accuracy for chemistry and solid-state physics, Physical Chemistry Chemical Physics 14, 16187 (2012).

70 O. A. Vydrov and G. E. Scuseria, Assessment of a long-range corrected hybrid functional, J. Chem. Phys. 125, 234109 (2006).

71 T. Yanai, D. P. Tew, and N. C. Handy, A new hybrid exchange–correlation functional using the coulomb-attenuating method (CAM-b3lyp), Chem. Phys. Lett. 393, 51 (2004).

72 R. Peverati and D. G. Truhlar, Improving the accuracy of hybrid meta-gga density functionals by range separation, The Journal of Physical Chemistry Letters 2, 2810 (2011).

73 R. Ditchfield, W. J. Hehre, and J. A. Pople, Self-consistent molecular-orbital methods. IX. an extended gaussian-type basis for molecular-orbital studies of organic molecules, J. Chem. Phys. 54, 724 (1971).
Projected Hybrids

74 W. J. Hehre, R. Ditchfield, and J. A. Pople, Self—consistent molecular orbital methods. XII. further extensions of gaussian—type basis sets for use in molecular orbital studies of organic molecules, J. Chem. Phys. 56, 2257 (1972).

75 T. H. Dunning, Gaussian basis sets for use in correlated molecular calculations. i. the atoms boron through neon and hydrogen, J. Chem. Phys. 90, 1007 (1989).

76 F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, Phys. Chem. Chem. Phys. 7, 3297 (2005).

77 J. A. Montgomery, M. J. Frisch, J. W. Ochterski, and G. A. Petersson, A complete basis set model chemistry. VI. use of density functional geometries and frequencies, J. Chem. Phys. 110, 2822 (1999).

78 J. J. Bao and D. G. Truhlar, Automatic active space selection for calculating electronic excitation energies based on high-spin unrestricted hartree–fock orbitals, Journal of Chemical Theory and Computation 15, 5308 (2019).

79 G. L. Manni et al., Multiconfiguration pair-density functional theory, J. Chem. Theory Comput. 10, 3669 (2014).

80 P. Sharma, J. J. Bao, D. G. Truhlar, and L. Gagliardi, Multiconfiguration pair-density functional theory, Ann. Rev. Phys. Chem. 72, 541 (2021).