

From densities to potentials: Benchmarking local exchange-correlation approximations

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Using the Kohn-Sham (KS) inversion method of Hollins *et al.* [*J. Phys.: Condens. Matter* **29**, 04LT01 (2017)], we invert densities from variational and diffusion quantum Monte Carlo (QMC) calculations to obtain benchmark QMC-KS potentials for a range of insulators and semiconductors, which we then compare to the KS potentials of popular density functional approximations (DFAs). Our results show that different DFAs yield similar electron densities, despite differences in their KS potentials, which originate primarily from the exchange and correlation contribution. We also find that the KS gap from the QMC density is typically larger than the KS gaps of most DFAs, with the exception of Hartree-Fock. Finally, the KS gap is sensitive to the inclusion of semicore states in the pseudopotentials, such that comparison with experiment should be done with caution.

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I. INTRODUCTION

Kohn-Sham (KS) density functional theory (DFT) [1,2] is ubiquitous in *ab initio* electronic structure calculations within condensed matter physics, chemistry, and materials science. In KS theory, an interacting system of electrons is mapped to an auxiliary noninteracting system of particles moving in a mean-field effective potential $v_s(\mathbf{r})$ that is constructed such that the ground-state densities of the interacting and noninteracting systems are the same. However, the exact exchange-correlation (XC) contribution $E_{xc}[\rho]$ to the KS energy functional is unknown, and by extension the exact XC contribution

$$v_{xc}[\rho](\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (1)$$

to the KS potential $v_s(\mathbf{r})$ is also unknown, necessitating approximations for both $E_{xc}[\rho]$ and $v_{xc}(\mathbf{r})$ in practice. Numerous density functional approximations (DFAs) [3–12] have been proposed over the decades, but the *direct* assessment of the accuracy of $E_{xc}[\rho]$ and $v_s(\mathbf{r})$ is a formidable challenge, not least because neither quantity is experimentally observable. Density inversion [13–27] offers a possible methodology to assess $v_s(\mathbf{r})$ and in particular $v_{xc}(\mathbf{r})$ by tackling the inverse KS problem, where for a given target density $\rho_t(\mathbf{r})$ one finds the KS potential $v_s(\mathbf{r})$ such that the ground-state density of the KS auxiliary system is equal to $\rho_t(\mathbf{r})$. Consequently, the inversion of numerically accurate densities enables one to gain insight into the behavior of the exact $v_s(\mathbf{r})$.

Quantum Monte Carlo (QMC) [28] methods are a well-established family of many-body techniques, which have played a historically significant role in the development of DFAs, notably in facilitating parametrizations [29,30] for the local density approximation (LDA) through QMC simulations of the homogeneous electron gas (HEG) [31]. Among such methods are the variational and diffusion Monte Carlo (VMC and DMC) methods. In the VMC method, electron configurations are sampled from the square modulus of a trial wave function using the Metropolis algorithm, with estimators of observables of interest being averaged over those configurations. The trial wave function contains free parameters that are optimized by minimizing either the energy expectation value or the variance of the energy. In the DMC method [31], a population of electron configurations (also known as walkers) is evolved according to the Schrödinger equation in imaginary time to project out the ground-state component of the trial wave function. Fermionic antisymmetry is maintained by fixing the complex phase of the DMC wave function at that of the VMC trial wave function.

In this work, we use the VMC and DMC methods to calculate the ground-state electronic densities of various semiconductors and insulators. We then invert these densities to find the KS potentials $v_s(\mathbf{r})$ that give rise to them in the ground state. Using the QMC densities and QMC-derived KS potentials as a benchmark, we assess the quality of various DFAs using a range of metrics, including KS band gaps, integrated absolute density differences, and integrated potential differences weighted by density differences. Following Burke and coworkers [32–35], we also analyze the total energy error of each DFA by examining the density-driven and functional error contributions.

The rest of this article is structured as follows. In Sec. II A, we provide the key details of our QMC calculations so that the benchmark densities used in this study can be critically assessed and reproduced. Section II B outlines our algorithm to invert densities and obtain the KS potential. We describe

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TABLE I. Calculated KS band gaps via inversion of the QMC density with various supercell sizes. The unsymmetrized (unsym) columns contain gaps obtained from inversion *without* explicit imposition of symmetry on the charge density. The symmetrized (sym) results are obtained via the appropriate imposition of symmetries on the charge density according to the symmetry operations of the crystallographic space group of the given material. Gaps are extrapolated (from unsymmetrized results) to infinite cell size according to Eq. (15). Experimental lattice parameters from Ref. [38] were used unless otherwise stated.

Material	KS band gap (eV)								Extrapolated
	111b cell		222b cell		333b cell		444b cell		
	unsym	sym	unsym	sym	unsym	sym	unsym	sym	
Si	0.550	0.627	0.713	0.748	0.783	0.798	0.799	0.815	0.812
Diamond	3.993	4.125	4.264	4.345	4.370	4.400	—		4.414
GaAs	1.115	1.212	1.293	1.309	1.346	1.354	—		1.368
Ge	0.123	0.267	0.315	0.334	0.360	0.366	—		0.379
NaCl	4.957	4.952	5.562	5.576	5.641	5.648	—		5.674
BaTiO ₃ ^a	3.390	3.553	3.252	3.288	3.219	3.242	—		3.206
SrTiO ₃ ^b	3.604	3.719	3.454	3.471	3.432	3.469	—		3.422
MnO ^c	2.570	2.595	2.914	2.914	2.943	2.952	—		2.952

^aLattice parameter from Refs. [69,70].

^bLattice parameters from Ref. [71].

^cLattice parameters from Ref. [72].

the errors and uncertainties in our charge densities in Sec. III. We compare our exact Kohn-Sham potential with other local potentials in Sec. IV, while the KS band gaps for each DFA along with the XC derivative discontinuity Δ_{xc} are described in Sec. V. Finally, we draw our conclusions in Sec. VI. We use Hartree atomic units (a.u.), in which the reduced Planck's constant $\hbar$, the electron mass m_e , the magnitude of the electronic charge e , and $4\pi\epsilon_0$ are 1 a.u., where ϵ_0 is the permittivity of free space.

II. THEORY AND COMPUTATIONAL DETAILS

A. Obtaining QMC charge densities

1. QMC calculations

The VMC and DMC calculations reported in this work were performed using the CASINO program [36], and the DFT calculations were carried out using the CASTEP plane-wave-basis-set code [37]. For the materials studied, we used experimental lattice parameters taken from Ref. [38] unless otherwise stated (see Table I). Trail-Needs (TN) Dirac-Fock pseudopotentials [39] were used to represent atomic cores. The s channel was chosen to be the local channel of the pseudopotential in each case to avoid possible issues with ghost states [40] that can arise due to the Kleinman-Bylander [41] representation of the pseudopotentials in plane-wave DFT calculations.

Our QMC trial wave functions were of Slater-Jastrow (SJ) form,

$$\Psi_T(\mathbf{R}) = S_{\uparrow}(\mathbf{R})S_{\downarrow}(\mathbf{R})\exp(J(\mathbf{R})), \quad (2)$$

where $\mathbf{R}$ is the $3N$ -dimensional electron configuration vector and $S_{\uparrow/\downarrow}(\mathbf{R})$ are Slater determinants of single-particle orbitals for spin-up and spin-down electrons. The Jastrow exponent $J(\mathbf{R})$ consisted of electron-electron, electron-ion, and electron-electron-ion polynomials, as well as electron-electron plane-wave expansions, with the coefficients being optimizable parameters [42]. The orbitals in the Slater

determinants were generated using CASTEP with the Perdew-Burke-Ernzerhof (PBE) [4] XC functional and re-represented in a B-spline (blip) basis for use in CASINO [43,44].

For greater accuracy in fixed-node DMC calculations for a particular system, Slater-Jastrow-backflow (SJB) [45,46] wave functions can be used. However, SJB wave functions are much more expensive to evaluate and, as shown in Fig. 1, the difference between SJ and SJB charge densities is small compared to finite-size errors at the system sizes for which backflow calculations are feasible. Hence, in practice, greater accuracy can be achieved by using an SJ wave function and studying larger simulation supercells. Throughout, the shorthand “*nnnb*” has been used to denote a calculation performed in a $n \times n \times n$ simulation supercell with the simulation-cell Bloch k -vector lying at the Baldereschi point. (See Sec. I of Supplemental Material [47] and Refs. [48,49] therein.)

Trial wave functions were optimized using two methods. The first was minimization of the variance of the local energy [50,51], which was used to efficiently optimize linear parameters in the Jastrow exponent only, providing an initial wave function. The second was minimization of the energy expectation value [52,53], which was used to optimize all free parameters and hence provide the final trial wave function.

2. Expectation value of the charge density

The DMC algorithm generates electron configurations distributed as the mixed distribution $|\Psi_T^*(\mathbf{R})\psi_{\text{DMC}}(\mathbf{R})|$, where $\psi_{\text{DMC}}(\mathbf{R})$ is the fixed-node ground-state wave function. The charge density operator

$$\hat{\rho}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \quad (3)$$

does not commute with the Hamiltonian, so the DMC mixed estimate of the charge density $\rho_{\text{DMC}}(\mathbf{r}) = \langle \Psi_T | \hat{\rho}(\mathbf{r}) | \psi_{\text{DMC}} \rangle / \langle \Psi_T | \psi_{\text{DMC}} \rangle$ is not equal to the pure estimate $\langle \psi_{\text{DMC}} | \hat{\rho}(\mathbf{r}) | \psi_{\text{DMC}} \rangle / \langle \psi_{\text{DMC}} | \psi_{\text{DMC}} \rangle$, unlike the case for the energy expectation value. We obtain a better approximation

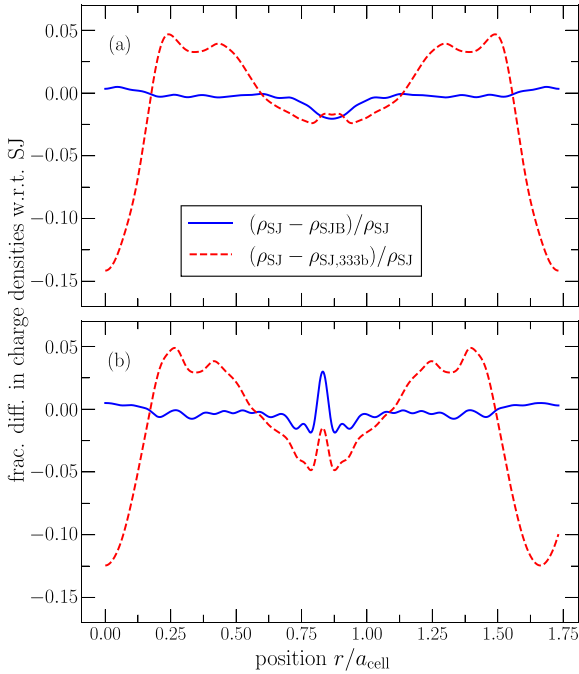


FIG. 1. Fractional difference between extrapolated estimates of the DMC charge density in a 111b cell with SJB and SJ trial wave functions (ρ_{SJB} and ρ_{SJ}), and between extrapolated estimates of the DMC charge density in 333b and 111b cells with an SJ trial wave function ($\rho_{\text{SJ,333b}}$ and ρ_{SJ}). Results are shown for (a) Si and (b) Ge. r is the distance along a straight line from the origin through the corner of the conventional unit cell, passing through its center. a_{cell} is the lattice parameter.

to the pure charge density using the extrapolated estimation method [54]. In this approach, we combine the VMC and DMC expectation values to eliminate systematic errors that are first order in the error $\Psi_{\text{T}} - \psi_{\text{DMC}}$ in the trial wave function by evaluating the extrapolated DMC charge density as

$$\rho(\mathbf{r}) \approx 2\rho_{\text{DMC}}(\mathbf{r}) - \rho_{\text{VMC}}(\mathbf{r}), \quad (4)$$

where $\rho_{\text{VMC}}(\mathbf{r}) = \langle \Psi_{\text{T}} | \hat{\rho}(\mathbf{r}) | \Psi_{\text{T}} \rangle / \langle \Psi_{\text{T}} | \Psi_{\text{T}} \rangle$ is the VMC charge density. The remaining error in the extrapolated density $\rho(\mathbf{r})$ is second order in the error in the trial wave function. In each case, two separate DMC calculations were performed, with time steps $\Delta t_1 = 0.04 \text{ Ha}^{-1}$ and $\Delta t_2 = 0.01 \text{ Ha}^{-1}$, and the DMC mixed estimate of the charge density in the limit of zero time step was calculated as

$$\rho_{\text{DMC}}(\mathbf{r}) = \frac{\rho_2(\mathbf{r}) - \rho_1(\mathbf{r})}{\Delta t_1 - \Delta t_2} \Delta t_1 + \rho_1(\mathbf{r}), \quad (5)$$

where ρ_1 and ρ_2 are the DMC mixed estimates of the charge density at time steps Δt_1 and Δt_2 , respectively. The DMC target walker population was varied in inverse proportion to the time step. Further details about the accumulation and preprocessing of densities for inversion are given in Sec. II of Ref. [47].

For completeness, we note that pure estimates of the DMC density could, in principle, be obtained without extrapolated estimation using the future-walking algorithm [55]. In practice, however, future walking introduces substantial statis-

tical noise, especially for the large supercells considered here. Reptation quantum Monte Carlo [56] provides another route to pure density estimates, but at significantly greater computational cost. Since the differences between extrapolated SJ and SJB densities are already small compared with finite-size effects, we do not expect the residual error from extrapolated estimation to affect our conclusions.

B. Inversion of charge densities

We follow the density inversion method of Refs. [57–61] implemented within the CASTEP code. At the start of the algorithm, the trial KS potential for spin channel σ $v_s^{\sigma(n=0)}$ is initialized to the PBE KS potential using the QMC charge density $\rho_{\text{QMC}}^{\sigma}$,

$$v_s^{\sigma(n=0)}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + v_H[\rho_{\text{QMC}}](\mathbf{r}) + v_{\text{xc}}^{\text{PBE}}[\rho_{\text{QMC}}](\mathbf{r}), \quad (6)$$

where each term on the right-hand side corresponds to the external (pseudopotential), Hartree, and PBE exchange-correlation (XC) potentials, respectively.

In a steepest descent algorithm, the potential $v_s^{\sigma}(\mathbf{r})$ at iteration n is updated according to

$$v_s^{\sigma(n+1)}(\mathbf{r}) = v_s^{\sigma(n)}(\mathbf{r}) - \epsilon \int d\mathbf{r}' \frac{\rho_{\text{QMC}}^{\sigma}(\mathbf{r}') - \rho_v^{\sigma(n)}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}. \quad (7)$$

Here, $\rho_v^{\sigma(n)}$ is the density of $v_s^{\sigma(n)}(\mathbf{r})$ at iteration n calculated via

$$\rho_v^{\sigma(n)}(\mathbf{r}) = \sum_i^{\text{occ}} \sum_{\mathbf{k}} f_{i\mathbf{k}} w_{\mathbf{k}} |\phi_{i\mathbf{k}}^{\sigma}(\mathbf{r})|^2. \quad (8)$$

The parameter $\epsilon > 0$ controls the rate of descent. The orbitals at each band i and k point $\mathbf{k}$, $\{\phi_{i\mathbf{k}}^{\sigma}\}$, and occupancies $f_{i\mathbf{k}}$ and weights $w_{\mathbf{k}}$ are obtained by solving the (spin-)KS equations

$$(-\frac{1}{2}\nabla^2 + v_s^{\sigma(n)}(\mathbf{r}))\phi_{i\mathbf{k}}^{\sigma(n)}(\mathbf{r}) = \varepsilon_{i\mathbf{k}}\phi_{i\mathbf{k}}^{\sigma(n)}(\mathbf{r}). \quad (9)$$

This procedure is repeated until the Coulomb energy

$$U = \sum_{\sigma} \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \frac{[\Delta\rho^{\sigma(n)}(\mathbf{r})][\Delta\rho^{\sigma(n)}(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|} \geq 0, \quad (10)$$

associated with the difference between the two densities, $\Delta\rho^{\sigma(n)}(\mathbf{r}) = \rho_{\text{QMC}}^{\sigma}(\mathbf{r}) - \rho_v^{\sigma(n)}(\mathbf{r})$, is sufficiently minimized.

In practice, the correction to the potential is done using the more efficient Fletcher-Reeves conjugate gradient algorithm [62], where the optimal value of ϵ is found using a parabolic line search to accelerate convergence. The Coulomb energy U is monitored over a set of four iterations and is deemed to be converged when the difference between the maximum and minimum value within this set is less than 10^{-8} Ha/atom . Note that, for consistency in the inversion of QMC densities in CASTEP, we used identical plane-wave cutoffs and k points to the original DFT calculations used to generate the Slater determinants for the QMC calculations.

The inversion scheme used in Refs. [57–61] is closely related to the earlier variational construction introduced in Ref. [63]. One considers the class of effective (noninteracting) Hamiltonians, $\hat{H}_v = \sum_i [-(1/2)\nabla_i^2 + v(\mathbf{r}_i)]$ with local potential v and ground state energies E_v , and minimizes the functional

$$T_{\Psi}[v] = \langle \Psi | \hat{H}_v | \Psi \rangle - E_v \quad (11)$$

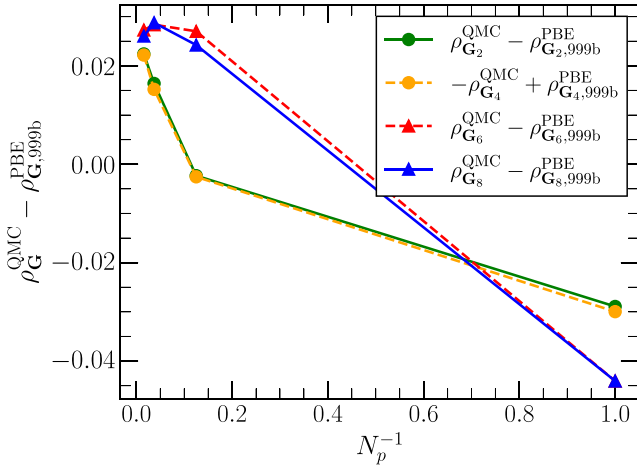


FIG. 2. Difference between the n th Fourier component of the density of Si as evaluated by QMC in a supercell containing N_p primitive cells with the supercell Bloch vector at the Baldereschi MVP ($\rho_{G,n}^{QMC}$) and the n th Fourier component of the density as evaluated by PBE using a $9 \times 9 \times 9$ k -point grid centered on the Baldereschi MVP ($\rho_{G,999b}^{PBE}$), plotted against the reciprocal of N_p . The $\{\rho_G\}$ are indexed in order of increasing $|\mathbf{G}|$; $\rho_{G,2}^{QMC}$ and $\rho_{G,4}^{QMC}$ are symmetry equivalent, as are $\rho_{G,6}^{QMC}$ and $\rho_{G,8}^{QMC}$. The differences between the symmetry-equivalent Fourier coefficients are indicative of the random errors in the QMC results.

over the effective potential v for a fixed many-body ground state Ψ yielding the target density [here $\rho_{QMC}(\mathbf{r})$]. This leads to the functional derivative

$$\frac{\delta T_\Psi[v]}{\delta v(\mathbf{r})} = \rho_{QMC}(\mathbf{r}) - \rho_v(\mathbf{r}), \quad (12)$$

with the update step given by the same functional derivative, or for improved convergence, the step in Eq. (7). The functional derivative in Eq. (12) is the negative of that of the Lieb functional [64]

$$F_L[\rho] = \sup_{v(\mathbf{r})} \left\{ E_v - \int \rho(\mathbf{r})v(\mathbf{r}) d\mathbf{r} \right\}, \quad (13)$$

so minimizing $T_\Psi[v]$ is equivalent to maximizing $F_L[\rho]$ in Eq. (13) (see also Ref. [65]). Further discussion of the two variational principles is given by Irons *et al.* [66], while inversion via the Lieb functional is discussed in Ref. [67]. The Coulomb-metric update in Eq. (7) is also closely related to the Zhao-Morrison-Parr (ZMP) method [15], although ZMP is usually formulated as a penalty approach involving the Fermi-Amaldi potential. See Ref. [59] for a discussion of our approach versus the ZMP method. We refer the reader to Ref. [68] for a further comparison of inversion methods.

III. ERRORS IN THE CHARGE DENSITY

A. Finite-size effects

Finite-size effects are a source of systematic error in explicitly correlated methods such as QMC.

In Fig. 2, we plot the differences between QMC- and PBE-calculated Fourier coefficients ρ_G of the density for the smallest nonzero shells of reciprocal-lattice vectors in Si. We focus on these small- $|\mathbf{G}|$ components because they are

the largest and hence the most sensitive to finite-size bias, while the differences between symmetry-equivalent coefficients provide a visual estimate of the residual statistical error. For reproducibility, the explicit coordinates of these reciprocal-lattice vectors are given in Table S2 of Ref. [47]. The QMC results are obtained in different supercells, while the PBE results are obtained using a fine k -point grid. Random errors in the QMC results are small compared to finite-size errors, as shown by the similarity of symmetry-equivalent Fourier coefficients at each system size. Furthermore, for sufficiently large supercells it is clear that finite-size errors in the Fourier coefficients are small compared with the difference between the QMC and PBE results.

Systematic finite-size effects in the total energy per primitive cell scale asymptotically as $\mathcal{O}(N_p^{-1})$ [73]. Therefore the total energy per primitive cell can be extrapolated to infinite system size according to

$$E_{N_p} = E_\infty + \frac{c}{N_p}, \quad (14)$$

where $\{E_{N_p}\}$ is the total energy per primitive cell obtained from a computational cell consisting of N_p primitive cells, c is a fitting parameter, and E_∞ is the energy per primitive cell in the thermodynamic limit. We excluded “supercells” consisting of a single primitive cell from the fit. A similar fit can be performed for the KS band gaps (the supercell analog of a HOMO-LUMO gap), which are obtained indirectly from the density via inversion followed by a band-structure calculation. For each computational supercell containing N_p primitive cells, we first calculate the QMC density $\rho_{N_p}(\mathbf{r})$, invert it to obtain the KS potential $v_s(\mathbf{r})$, and then perform a band-structure calculation using the Monkhorst-Pack grid commensurate with that supercell. Repeating this for each supercell yields the corresponding KS gaps $\{E_{g,N_p}\}$, which we fit according to

$$E_{g,N_p} = E_{g,\infty} + \frac{\tilde{c}}{N_p}, \quad (15)$$

where $\tilde{c}$ is a fitting parameter and $E_{g,\infty}$ is the extrapolated KS gap. Note that, as mentioned in Sec. II B, if the QMC density is generated in a supercell consisting of N_p primitive cells, the inversion calculation is performed using the commensurate Monkhorst-Pack grid of $N_p k$ points, which was also used for the generation of the Slater determinant in the QMC trial wave function. Furthermore, since the Monkhorst-Pack grid is not centered on the Γ point but on the Baldereschi MVP, we do not impose time-reversal symmetry on the Monkhorst-Pack grid.

Figure 3 shows that the finite-size trend in the KS gap can be controlled systematically by increasing the computational supercell used for the QMC calculation (and, correspondingly, the Monkhorst-Pack grid used in the initial DFT and inversion calculations). In this sense, the finite-size effects in the KS gap are no more uncontrolled than those in the density itself. The practical advantage of working with the gap is that it is a single scalar quantity, whereas the density is represented by many thousands of Fourier components.

The KS band gaps for each supercell and system studied are given in Table I along with the extrapolated KS band gap. We show an example of this extrapolation for Si in Fig. 3,

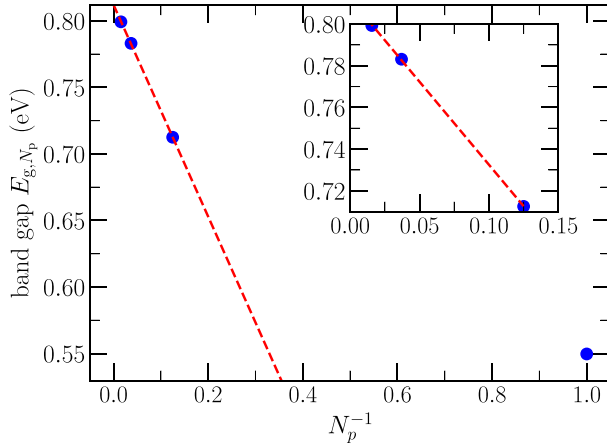


FIG. 3. KS band gaps $E_{g,N}$ calculated via inversion of the Si density obtained from various QMC simulation supercells consisting of N_p primitive cells (equivalently, the number of k points within the inversion/DFT calculation). The dashed red line shows a linear fit of the gap $E_{g,N}$ as a function of N_p^{-1} , yielding an extrapolated band gap of 0.81 eV at infinite system size.

where the extrapolated KS band gap is 0.81 eV, while in Fig. 4 we show the calculated KS band structure obtained via inversion of the QMC density from a computational supercell consisting of N_p primitive cells. As a general rule, calculations

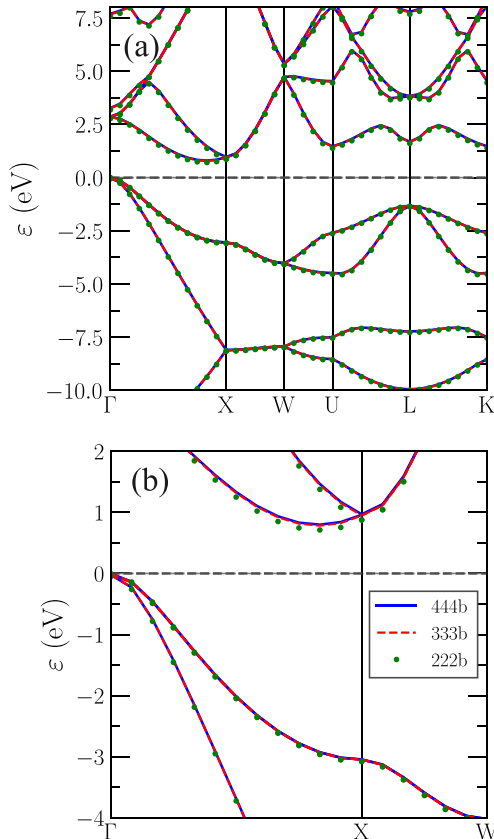


FIG. 4. (a) Calculated KS band structure for Si using the inverted density from various supercells. (b) shows the same band structure but zoomed in around the band gap.

performed in the primitive cell are dominated by finite-size errors and thus are outliers. However, one can see that the KS gaps $E_{g,N}$ obtained from the 222b, 333b, and 444b supercells vary linearly with N_p^{-1} . We assume this linear scheme holds for the other systems studied such that $E_{g,\infty}$ can be obtained via extrapolation from 222b and 333b cells.

B. Statistical errors

Ideally, the random errors of the simulation should be considerably smaller than the systematic finite-size errors. The random errors in the Fourier components of the density are correlated. In principle, one could calculate the covariance matrix between the Fourier components $\rho_{\mathbf{G}}$. However, given that the number of Fourier components is of the order of tens of thousands, the calculation of the covariance matrix would be computationally demanding, and the propagation of statistical errors to the density-dependent KS gap would also be very challenging, as it would require partial derivatives of the gap with respect to each $\rho_{\mathbf{G}}$. In practice, the simplest, albeit computationally demanding, approach for obtaining error bars on quantities derived from the charge density, such as the inverted-density KS band gap, is to repeat the entire calculation several times and take the mean and the standard error of the mean of the results obtained.

Alternatively, one can obtain a rough estimate of the random errors in the charge density by comparing Fourier components $\rho_{\mathbf{G}}$ that ought to be identical under the symmetry of the crystal, as done in Fig. 2. Due to the stochastic nature of the Monte Carlo techniques, no symmetries are explicitly imposed on the charge density during VMC and DMC calculations. However, any expected symmetries in the charge density should still arise up to statistical error. By examining the charge density Fourier components $\rho_{\mathbf{G}}$, one can instead verify that the expected symmetries in the densities are present up to statistical error.

Therefore, as a preliminary step, one can ensure that the Fourier components of the charge density $\rho_{\mathbf{G}}$ satisfy the expected symmetries of a given system up to a certain numerical threshold. In particular, since the density $\rho(\mathbf{r})$ is a real function, its Fourier components satisfy $\rho_{\mathbf{G}}^* = \rho_{-\mathbf{G}}$. Furthermore, when the crystal possesses inversion symmetry, this property is shared by the density. In reciprocal space, the Fourier components thus satisfy $\rho_{-\mathbf{G}} = \rho_{\mathbf{G}}$. This identity, along with the previous one for the Fourier components of a real function, implies that the Fourier components themselves must be real, satisfying the relation

$$\rho_{\mathbf{G}}^* = \rho_{-\mathbf{G}} = \rho_{\mathbf{G}}. \quad (16)$$

To check whether inversion symmetry is satisfied, we compare Fourier components at reciprocal lattice vectors $\pm\mathbf{G}$ according to

$$|\rho_{\mathbf{G}} - \rho_{-\mathbf{G}}| \leq \epsilon_{\text{atol}} + \epsilon_{\text{rtol}} \times |\rho_{-\mathbf{G}}|, \quad (17)$$

where ϵ_{atol} is the absolute tolerance and ϵ_{rtol} is the relative tolerance. For systems with inversion symmetry, this inequality was satisfied with $\epsilon_{\text{atol}} = 10^{-6}$ a.u. and $\epsilon_{\text{rtol}} = 10^{-5}$.

Furthermore, since the input target density for the inversion is ultimately done on a real-space rectilinear grid, the real-space density $\rho_{\text{QMC}}(\mathbf{r})$ can be checked by symmetrizing it

according to the symmetry operations of the corresponding space group.

The integrated absolute difference (IAD) between the symmetrized $\rho_{\text{QMC}}^{\text{sym}}(\mathbf{r})$ and unsymmetrized density $\rho_{\text{QMC}}(\mathbf{r})$ is defined as

$$\text{IAD} = \frac{1}{N_r} \sum_{n=1}^{N_r} |\rho_{\text{QMC}}(\mathbf{r}_n) - \rho_{\text{QMC}}^{\text{sym}}(\mathbf{r}_n)|, \quad (18)$$

where N_r is the number of real-space grid points $\mathbf{r}_n$. We found that the mean IAD per electron averaged over all materials and simulation cells was ~ 0.022 .

To further check the KS potentials, we performed an inversion of the symmetrized density $\rho_{\text{QMC}}^{\text{sym}}$ and compared the calculated KS band structures with the band structures obtained from inversion of the density without the explicit imposition of symmetry. Note that the running density $\rho_v(\mathbf{r})$ (i.e., density for the potential at each iteration) in this inversion calculation is also symmetrized along with the KS potential $v_s(\mathbf{r})$ at each iteration. The Coulomb energy [see Eq. (10)] is likewise calculated from both the symmetrized $\rho_{\text{QMC}}(\mathbf{r})$ and $\rho_v(\mathbf{r})$. The calculated KS gaps from the inversion of the symmetrized QMC density $\rho_{\text{QMC}}^{\text{sym}}(\mathbf{r})$ and unsymmetrized density $\rho_{\text{QMC}}(\mathbf{r})$ are given in Table I. The difference between the band structures can be quantified using the mean absolute eigenvalue difference (MAED)

$$\text{MAED} = \frac{1}{N_b N_k} \sum_{i,\mathbf{k}} |\varepsilon_{i\mathbf{k}} - \varepsilon_{i\mathbf{k}}^{\text{sym}}|, \quad (19)$$

where N_b and N_k are the numbers of bands and $\mathbf{k}$ -points, respectively, in the band structure, and the $\{\varepsilon_{i\mathbf{k}}^{\text{sym}}\}$ are the eigenvalues of the KS Hamiltonian with potential $v_s(\mathbf{r})$ obtained from $\rho_{\text{QMC}}^{\text{sym}}(\mathbf{r})$. Naturally, if running a spin-polarized calculation, we average over all spins as well with the denominator in the prefactor changing from $N_b N_k \rightarrow 2N_b N_k$. We found the MAED to be of the order of 10^{-2} eV with the averaged MAED over all systems and computational supercells being 4×10^{-2} eV.

We observed a larger deviation between the symmetrized and unsymmetrized QMC densities obtained from a single primitive cell. As previously discussed, the error in this density also has a contribution from systematic finite-size effects which are particularly significant for calculations in a single primitive cell (see Table I). If we exclude these densities from the calculation of the mean IAD, we find that the mean IAD per electron is reduced to ~ 0.01 while the MAED is reduced to 2×10^{-2} eV. The small difference between the symmetrized and unsymmetrized calculations, particularly for QMC densities in larger supercells, is encouraging, suggesting that the random error in the calculation is small and that finite-size error is more significant.

IV. ASSESSING DENSITIES AND LOCAL POTENTIALS

A. Behavior of exchange-correlation potentials

Using the QMC density obtained with the largest computational supercell as a benchmark, we now assess the quality of densities and XC potentials from various density functional approximations (DFAs) at different rungs of Jacob's ladder [74], namely the LDA, PBE [a generalized gradient approx-

imation (GGA)], regularized SCAN (rSCAN; a meta-GGA), and HSE06 (a hybrid DFA), in addition to Hartree-Fock (HF). We note that meta-GGAs, hybrid DFAs, and HF are explicit functionals of the single-particle orbitals and are thus non-local, implicit functionals of the density; in hybrids and HF, the nonlocality arises from the Fock exchange term and in meta-GGAs due to terms involving the kinetic energy density. Such DFAs can be treated either in a KS scheme via the optimized effective potential (OEP) method [75–77], or using a generalized Kohn-Sham (GKS) scheme [78–80] with a nonlocal effective potential.

For these nonlocal DFAs, we note that a KS potential $v_s(\mathbf{r})$ can also be obtained by inverting the GKS target density $\rho_{\text{GKS}}(\mathbf{r})$. In particular, as pointed out in Refs. [57,58], and [61], the exchange-only potential obtained by inversion of the HF density, dubbed the local Fock exchange (LFX) potential $v_x^{\text{LFX}}(\mathbf{r})$ in these references, is similar to the exchange-only OEP. Furthermore, it is expected that the XC potential $v_{xc}(\mathbf{r})$ [referred to as the local exchange-correlation (LXC) potential in Ref. [61]] obtained from the inversion of any GKS density will be similar to that obtained via the OEP method (except possibly in strongly correlated systems). A thorough discussion and comparison of GKS, OEP, and KS inversion calculations (referred to as inv-OEP) can be found in Ref. [81]. Alternatively, as shown by Garrick *et al.* [82] in the case of hybrid functionals, one can invert a GKS density directly to recover the corresponding nonlocal GKS effective potential.

In order to facilitate a like-for-like comparison, it is crucial that the external potential for each calculation is identical, so that any differences arise solely due to the DFA's XC functional. Therefore, to ensure consistency, all calculations were carried out using the same TN pseudopotential (including the same local angular momentum channel).

In Fig. 5, we compare the densities of each method along with the (local) $v_{xc}(\mathbf{r})$ in Si. The density is plotted along a path through the unit cell shown by the red arrows in Fig. 5(a). As one might expect, the potential is deeper (more negative) where the density is higher, for instance in the bonding region as highlighted by the cyan and green isosurfaces in Fig. 5(a). Moreover, it can be seen that the HF density is overlocalized compared to the QMC density, particularly in the bonding region along the bond axis from the Si atom at $(1, 1, 1) = (0, 0, 0)$ to the other Si atom at $(1/4, 1/4, 1/4)$. The LFX potential obtained from the inversion of the HF density is consequently too deep. By contrast, the other DFAs have a slight delocalization error in their densities and correspondingly shallower $v_{xc}(\mathbf{r})$ than $v_{xc}^{\text{QMC}}(\mathbf{r})$ in this region. The spikes observed in the XC potential near ions appear to be a pseudopotential artifact due to the valence charge density tending to zero inside the core region of the pseudopotential. As discussed in Appendix B for the PBE potential $v_{xc}^{\text{PBE}}(\mathbf{r})$, this effect arises even in standard DFT calculations using the latest CASTEP on-the-fly norm-conserving (NCP19) pseudopotentials [83,84] when nonlinear core corrections are *not included*; nonlinear core corrections are also absent in the TN pseudopotentials. Similar spikes have been observed in the inversion calculations of auxiliary-field QMC densities by Aouina and coworkers in Refs. [25,26], which used optimized norm-conserving pseudopotentials (ONCVSP) without

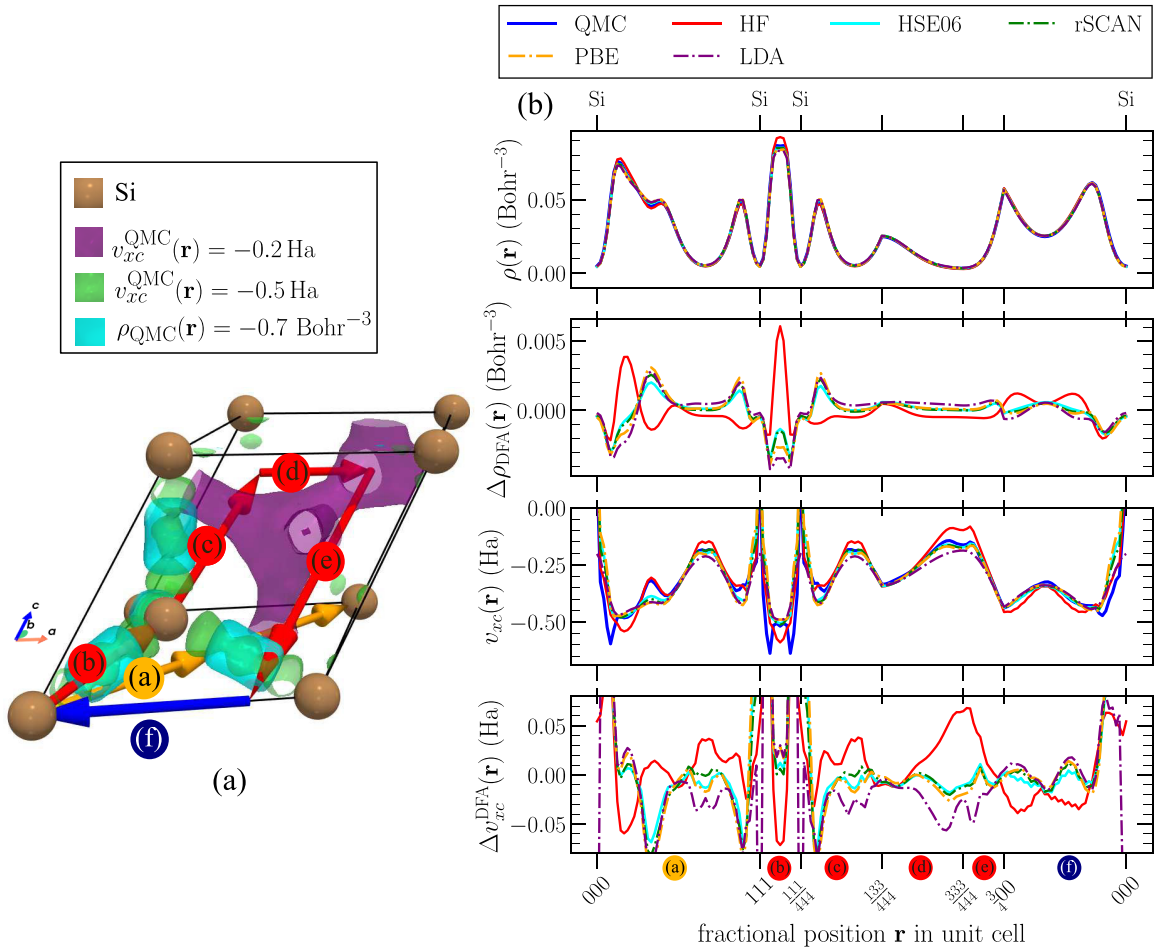


FIG. 5. (a) Isosurfaces of the (unsymmetrized) QMC density $\rho_{\text{QMC}}(\mathbf{r})$ and $v_{xc}^{\text{QMC}}(\mathbf{r})$ in bulk Si. (b) In the first and third panels, the density of each method $\rho(\mathbf{r})$ and the corresponding $v_{xc}(\mathbf{r})$, respectively, are plotted along the path through the unit cell shown by the colored arrows in (a) (the colors of the arrows help distinguish portions of the path). The respective portion of the path is indicated by the colored circles in (a) and on the x axis of (b). In the second and fourth panels, we plot the density difference $\Delta\rho_{\text{DFA}}(\mathbf{r})$ and the XC potential difference $\Delta v_{xc}^{\text{DFA}}(\mathbf{r})$ from the respective QMC results for various DFAs. The isosurface for the density has been chosen to coincide with regions of high electron density associated with bonding.

nonlinear core corrections generated according to the method of Hamann [85]. The corresponding results for NaCl are shown in Fig. 6.

We observed similar behavior in other diamondlike crystal structure semiconductors, namely diamond, GaAs, and Ge as shown in Fig. 7. It turns out, however, that the results for GaAs and Ge have a significant systematic error due to the inclusion of atomic semicore electronic states within the pseudopotential, treating them as core states. We discuss this in further detail specifically for the inversion of HF densities in Appendix A. Nonetheless, the analysis in our work here remains valid given that we have used the same pseudopotential (external potential). Plots of $v_{Hxc}(\mathbf{r})$ are provided in Ref. [47] for Si and NaCl in Figs. S8 and S9.

In systems where the (pseudovalence) charge density is very low (nearly zero) over extended spatial regions, such as in ionically bonded NaCl, the QMC KS potential $v_{xc}^{\text{QMC}}(\mathbf{r})$ undergoes oscillations; no smoothing or other post-processing has been applied to the potentials shown in this work. These oscillations are reminiscent of those reported in Ref. [86],

although in that case they arose from the use of a localized Gaussian-type orbital basis rather than from statistical noise in the target density. On the other hand, $v_{xc}^{\text{QMC}}(\mathbf{r})$ is well-behaved elsewhere and we note that similar behavior was observed in Ref. [26]. For a density that is strictly zero in a region, or even not strictly positive everywhere in the region, the Hohenberg-Kohn (HK) theorem [i.e., the one-to-one correspondence between $v_s(\mathbf{r})$ and the ground state density $\rho(\mathbf{r})$] breaks down inside the region, since the HK theorem requires a density that is nonzero almost everywhere. A similar result is obtained in the inversion of BaTiO $_3$ and SrTiO $_3$ as shown in Figs. 8(a) and 8(b), respectively. A further discussion of this point can be found in Refs. [87–90]. In our case, the density is not strictly zero in this region but numerically very small, and the convergence of the inversion algorithm in such regions is slow and can pose numerical challenges. This is demonstrated and discussed in Sec. III of Ref. [47]. Nonetheless, as can be seen in the inset in Fig. 8, the expected qualitative behavior is still observed in these low-density regions, where $v_{xc}^{\text{QMC}}(\mathbf{r})$ is deeper than the DFA XC potentials when

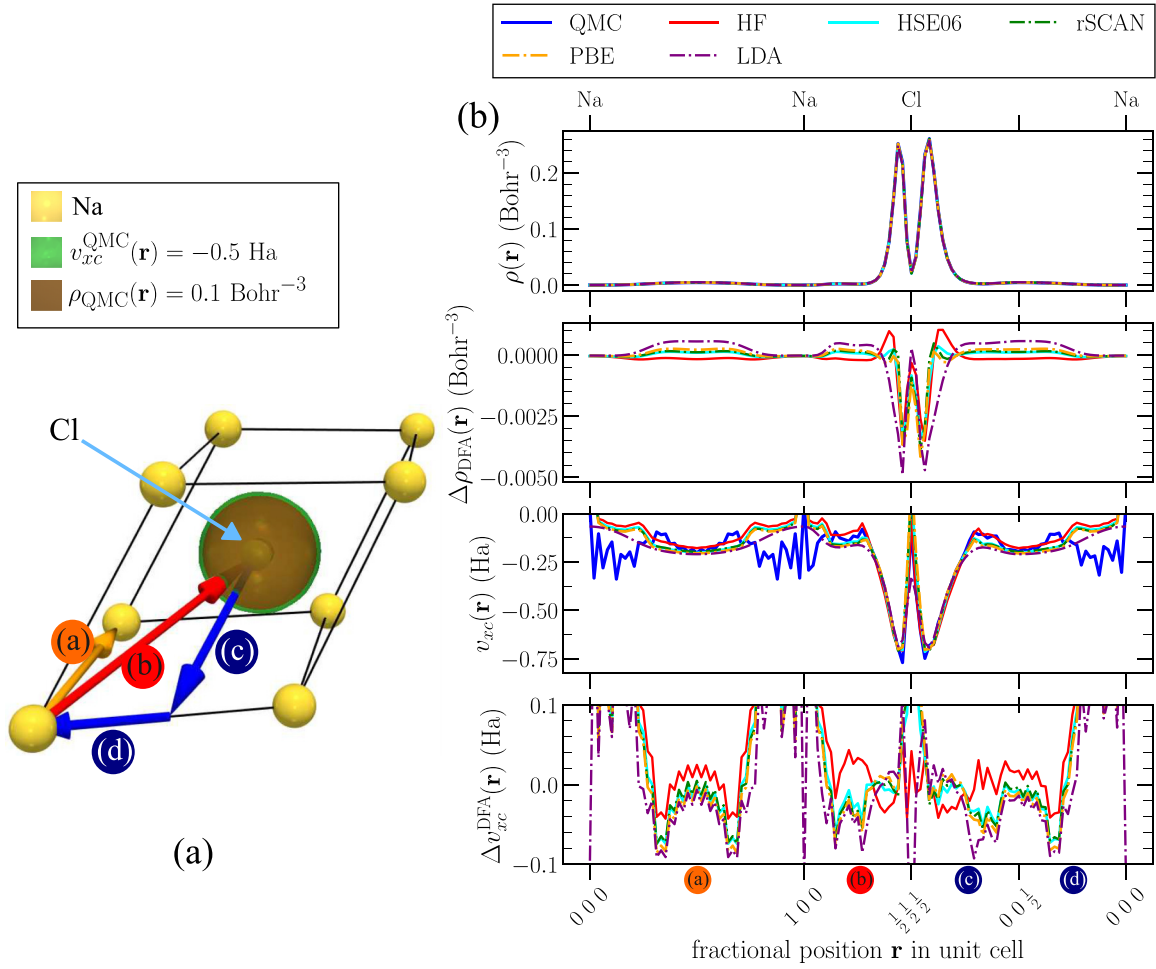


FIG. 6. Same as Fig. 5 for NaCl. Note that the Cl atom at the center of the cell is marked by the blue arrow. Isosurfaces have been chosen to coincide with regions of high electron density associated with bonding.

the QMC density is slightly larger than the DFAs' densities. This is also a good demonstration that even small differences in the density can lead to large differences in the KS potential [91,92].

In MnO, which exhibits antiferromagnetic ordering, we observed similar difficulties in converging the potential where the charge density is low, as shown in Fig. 9. For instance, near the Mn spin-down ion, $v_{xc}^{\uparrow}(\mathbf{r})$ exhibited severe oscillations [and similarly for $v_{xc}^{\downarrow}(\mathbf{r})$ near the Mn spin-up ion]. Outside of these regions, however, some more meaningful insight can be drawn from the behavior of the potential and the density. In particular, all DFAs considered in this work (with the TN pseudopotentials) overlocalize the electrons around the ions compared to the QMC density, leading to deeper potentials (as expected). Unfortunately, due to the hardness of the Mn pseudopotential and consequently the necessity for a relatively high plane-wave cutoff energy to converge the basis set, we were unable to run HF or HSE06 calculations for MnO.

B. Metrics for assessing densities and KS potentials

In order to gain more quantitative insight into the quality of these densities and potentials, we now define two metrics to quantify the “error” between the QMC density/potential

obtained via inversion and that of each DFA. A simple comparison of densities can be carried out using the integrated absolute error (IAE) per electron, defined in a similar fashion to the IAD in Eq. (18),

$$\text{IAE} = \frac{1}{N_r} \sum_{n=1}^{N_r} |\rho_{\text{QMC}}(\mathbf{r}_n) - \rho_{\text{DFA}}(\mathbf{r}_n)|. \quad (20)$$

Additionally, given the one-to-one correspondence between the density and the Kohn-Sham potential, we define a second metric to compare both a pair of densities and their corresponding Kohn-Sham potentials simultaneously:

$$\mathcal{E} = - \sum_{\sigma} \int d\mathbf{r} (\rho_{\text{DFA}}^{\sigma}(\mathbf{r}) - \rho_{\text{QMC}}^{\sigma}(\mathbf{r})) \times (v_{\text{DFA}}^{\sigma}(\mathbf{r}) - v_{\text{QMC}}^{\sigma}(\mathbf{r})) > 0, \quad (21)$$

which for a numerical density stored on a grid of size N_r is evaluated via

$$\mathcal{E} = - \sum_{\sigma} \frac{1}{N_r} \sum_{n=1}^{N_r} (\rho_{\text{DFA}}^{\sigma}(\mathbf{r}_n) - \rho_{\text{QMC}}^{\sigma}(\mathbf{r}_n)) \times (v_{\text{DFA}}^{\sigma}(\mathbf{r}_n) - v_{\text{QMC}}^{\sigma}(\mathbf{r}_n)). \quad (22)$$

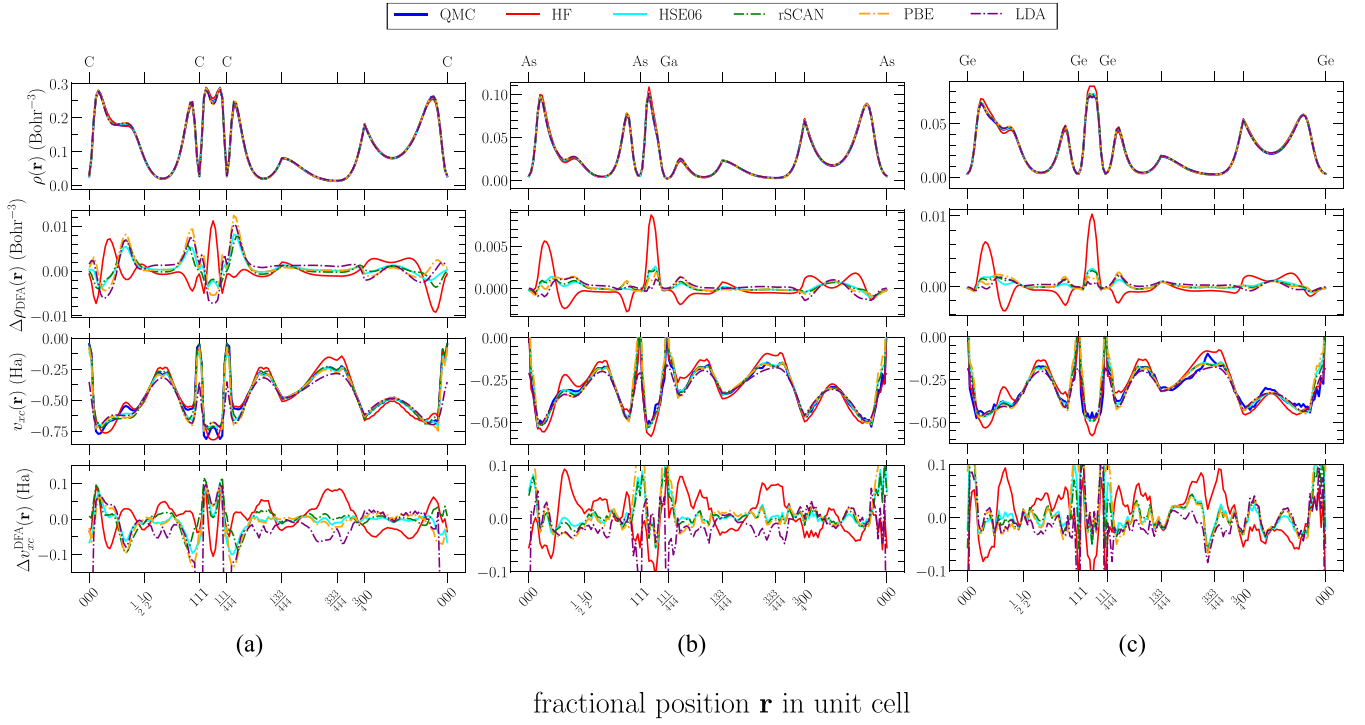


FIG. 7. Same as Fig. 5(b) for bulk (a) diamond, (b) GaAs, and (c) Ge. Note that the same path has been used as for bulk Si, shown in Fig. 5(a).

The use of the quantity $\mathcal{E}$ (with units of energy) is motivated by the proof of the HK theorem, see, e.g., Theophilou's Ref. [93], and has the physical interpretation that a region within which the potential is deeper must have a correspondingly higher density. An advantage of this metric over a simple integrated difference in potentials similar to the IAE in Eq. (20) is the appropriate weighting of the potential; in particular, this ensures the oscillations in the QMC potential observed in the low-density regions in some systems do not significantly contribute to the overall value of the metric. As discussed in Ref. [88], such oscillations in the KS potential do not pose a significant problem given that there is no charge density to "see" these oscillations. In addition, we note that this $\mathcal{E}$ is invariant under constant shifts in the potential(s), or equivalently an overall constant shift in the potential difference V_0

$$\begin{aligned}\tilde{\mathcal{E}} &= - \sum_{\sigma} \int d\mathbf{r} \Delta\rho^{\sigma}(\mathbf{r}) (\Delta v^{\sigma}(\mathbf{r}) + V_0) \\ &= - \sum_{\sigma} \left[\int \Delta\rho^{\sigma}(\mathbf{r}) \Delta v^{\sigma}(\mathbf{r}) d\mathbf{r} + V_0 \int \Delta\rho^{\sigma}(\mathbf{r}) d\mathbf{r} \right] = \mathcal{E},\end{aligned}\quad (23)$$

where $\Delta\rho^{\sigma}(\mathbf{r}) = \rho_{\text{DFA}}^{\sigma}(\mathbf{r}) - \rho_{\text{QMC}}^{\sigma}(\mathbf{r})$ and $\Delta v^{\sigma}(\mathbf{r}) = v_{\text{DFA}}^{\sigma}(\mathbf{r}) - v_{\text{QMC}}^{\sigma}(\mathbf{r})$. Here, we make use of the fact that the integral on the last line of Eq. (23) vanishes since each density integrates to N electrons, thus $\int \Delta\rho^{\sigma}(\mathbf{r}) d\mathbf{r} = 0$, hence Eq. (23) reduces to the original definition in Eq. (21).

We have compared the densities from QMC with various DFAs using both the IAE and $\mathcal{E}$ in Table II. In order to facilitate a like-for-like comparison between systems, we have

quoted the value for each metric per electron. No finite-size correction was applied to either the charge density or the potential obtained from inversion; instead, we used the density obtained from the QMC calculation performed with the largest computational supercell.

Considering the IAE first, as one might expect, the performance of the LDA ranges from being comparable in accuracy to other functionals from higher rungs of Jacob's ladder to being the worst performing functional, particularly in Si and NaCl. At the other end of the spectrum, HF has, by some margin, the largest error out of all the DFAs studied. As seen in our results, this can be attributed to errors which arise from failing to account for correlation, and thus an overlocalization with respect to the QMC (or more generally exact) density. The functional with the most accurate density according to this metric (groundstate density being closest to the QMC density) across the widest range of systems is rSCAN, performing better than the HSE06 functional, despite its lower computational cost. Next is PBE, followed by LDA, with the worst functional in this metric being HF.

Turning our attention now to the energy metric $\mathcal{E}$, one might expect that the error in the density would be correlated with the error in the potential, resulting in similar trends to those observed in the IAEs. However, this turns out not to be the case, even in systems with similar chemical environments.

For instance, according to the $\mathcal{E}$ metric, in BaTiO₃ and SrTiO₃, HF and then LDA are superior to PBE, but still worse than rSCAN and HSE06. Furthermore, in some systems like MnO, rSCAN appears to have a worse potential despite having a more accurate density as evidenced by the larger value of $\mathcal{E}$ despite the lower IAE. Overall, according to the metric

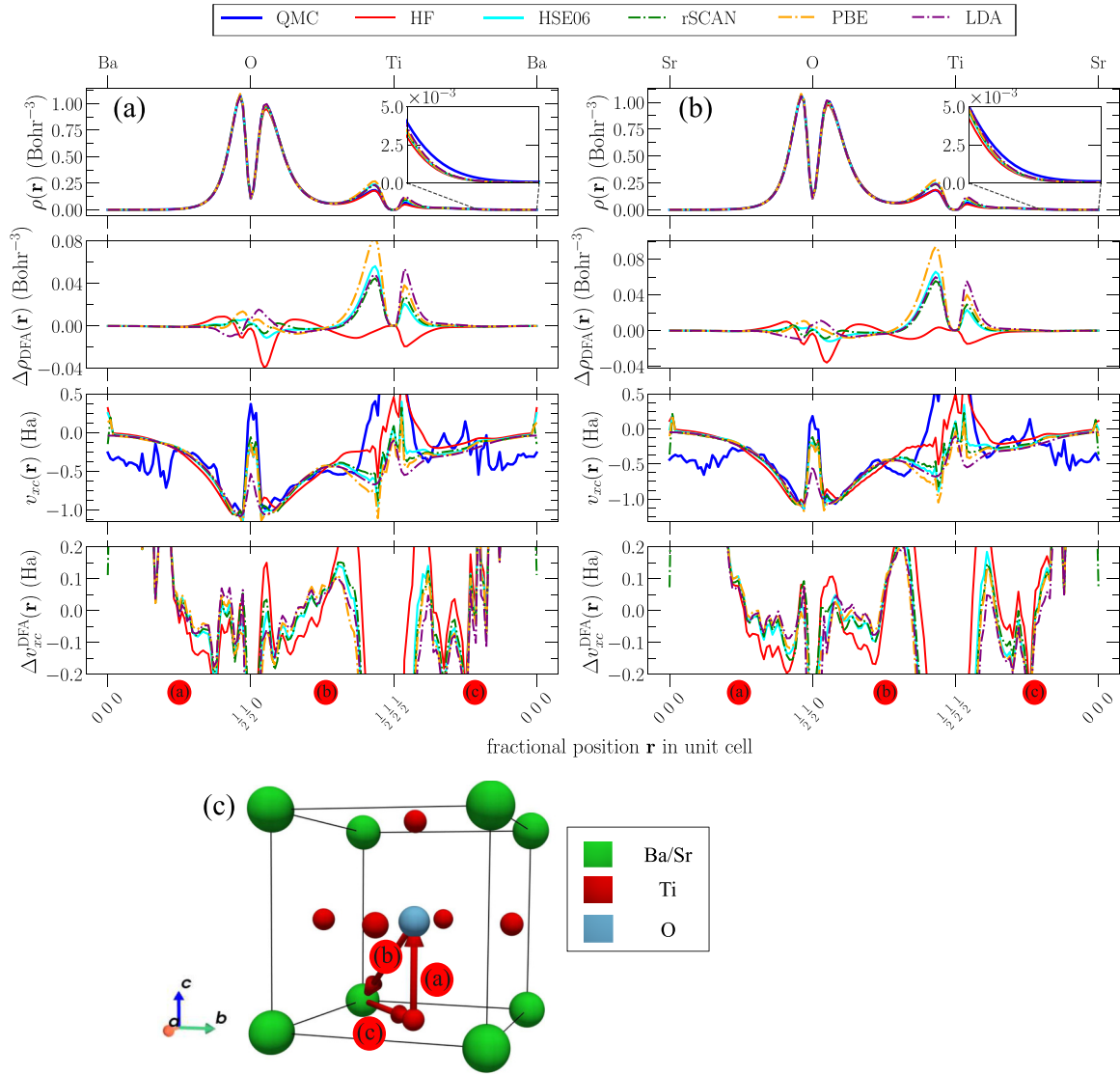


FIG. 8. Top panel: Comparison of QMC $\rho_{\text{QMC}}(\mathbf{r})$ and DFA $\rho_{\text{DFA}}(\mathbf{r})$ densities along a path through the unit cell for (a) BaTiO_3 and (b) SrTiO_3 ; second panel: density difference of each DFA along the path $\Delta\rho_{\text{DFA}}(\mathbf{r})$; third panel: corresponding $v_{xc}(\mathbf{r})$ for QMC and each DFA; and fourth panel: difference in XC potential $\Delta v_{xc}^{\text{DFA}}(\mathbf{r})$ from the $v_{xc}^{\text{QMC}}(\mathbf{r})$. The path taken through the unit cell is shown in (c). The insets show the density in low-density region.

$\mathcal{E}$, the best functionals are rSCAN together with HSE06, followed by LDA, PBE, and finally HF.

C. Density-functional error analysis

In addition to the density and the potential, we can also assess the error in the total energy as a result of the approximation for E_{xc} in order to gain further insight into the successes (or failures) of DFAs. We follow the error analysis scheme of Burke and coworkers [32–35,94] for the total energy error of a particular DFA,

$$\Delta E_{\text{DFA}} \doteq E_{\text{DFA}}[\rho_{\text{DFA}}] - E_{\text{exact}}[\rho_{\text{exact}}], \quad (24)$$

where $\rho_{\text{exact}}(\mathbf{r})$ is the exact density and $\rho_{\text{DFA}}(\mathbf{r})$ is the density obtained via a self-consistent calculation using the DFA; $E_{\text{DFA}}[\rho_i]$ is the DFA total energy evaluated at the density $\rho_i(\mathbf{r})$ and $E_{\text{exact}}[\rho_{\text{exact}}]$ is the exact total energy. Next, the total energy error is partitioned into two separate errors due to (i)

an inaccurate density [density-driven error (DE)] and (ii) an inaccurate XC energy functional [functional error (FE)],

$$\Delta E_{\text{DFA}} = \Delta E_{\text{FE}} + \Delta E_{\text{DE}}, \quad (25)$$

with

$$\Delta E_{\text{FE}} = E_{\text{DFA}}[\rho_{\text{exact}}] - E_{\text{exact}}[\rho_{\text{exact}}], \quad (26)$$

$$\Delta E_{\text{DE}} = E_{\text{DFA}}[\rho_{\text{DFA}}] - E_{\text{DFA}}[\rho_{\text{exact}}] < 0, \quad (27)$$

$\Delta E_{\text{DE}} < 0$ because $\rho_{\text{DFA}}(\mathbf{r})$ is the minimizing density of the functional $E_{\text{DFA}}[\rho]$. In our analysis, the exact density $\rho_{\text{exact}}(\mathbf{r})$ is approximated by the QMC density $\rho_{\text{QMC}}(\mathbf{r})$, while the exact energy $E_{\text{exact}}[\rho_{\text{exact}}]$ is taken to be the DMC energy extrapolated to zero time step and infinite system size. We extrapolate the DMC energy linearly to zero time step [36]. The zero-time-step extrapolated values for each supercell are then extrapolated to infinite system size using Eq. (14).

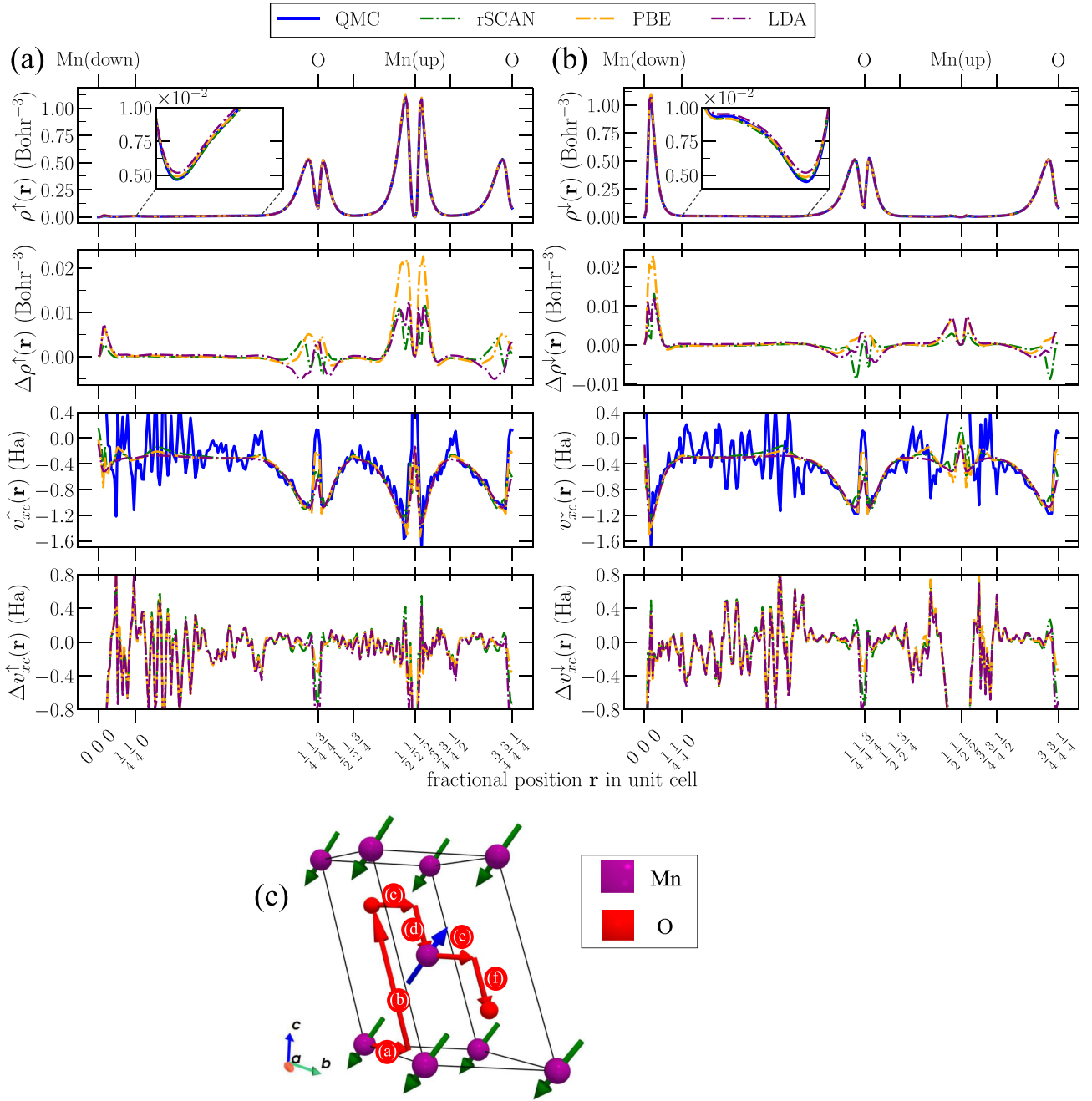


FIG. 9. Same as Fig. 5(b) for bulk MnO. The panels on the left show (a) spin-up quantities while the panels on the right are for (b) spin-down. The path taken through the unit cell is shown in (c).

To proceed, we distinguish between local/semilocal approximations (LDA/PBE) and nonlocal approximations (rSCAN/HSE06/HF). For the former, the application of Eqs. (26) and (27) is straightforward, but not for the latter. For example, in nonlocal approximations, $E_{\text{DFA}}[\rho_{\text{exact}}]$ must be obtained from an inversion of the QMC density with the appropriate nonlocal GKS equations, using the GKS orbitals, $E_{\text{DFA}}[\rho_{\text{exact}}] = E_{\text{DFA}}[\{\phi_i^{\text{GKS}}[\rho_{\text{exact}}]\}]$. However, in this work, we only perform a standard KS inversion of the QMC density with a local KS potential and obtain KS orbitals $\{\phi_i^{\text{KS}}[\rho_{\text{exact}}]\}$. To estimate the FE [Eq. (26)] in terms of the calculated quan-

ties, we write

$$\Delta E_{\text{FE}} = \Delta E_{\text{DFA}}^{\text{NL}}[\rho_{\text{exact}}] + E_{\text{DFA}}[\{\phi_i^{\text{KS}}[\rho_{\text{exact}}]\}] - E_{\text{exact}}[\rho_{\text{exact}}], \quad (28)$$

where

$$\Delta E_{\text{DFA}}^{\text{NL}}[\rho] \doteq E_{\text{DFA}}[\{\phi_i^{\text{GKS}}[\rho]\}] - E_{\text{DFA}}[\{\phi_i^{\text{KS}}[\rho]\}] \leq 0 \quad (29)$$

is the DFA's nonlocality energy at density $\rho(\mathbf{r})$ (see Ref. [61]). The KS orbitals $\{\phi_i^{\text{KS}}[\rho]\}$ are found by inverting the density ρ and are eigenstates of the resulting single-particle

TABLE II. Comparison of densities and corresponding Kohn-Sham potentials using the integrated absolute error (IAE) per electron and the energy difference $\mathcal{E}$ per electron (in mHa) as defined in Eq. (21). The density used as the QMC benchmark is taken from the calculation using the largest computational supercell,

Material	IAE per electron $\times 10^{-2}$					$\mathcal{E}$ (mHa)				
	LDA	PBE	rSCAN	HSE06	HF	LDA	PBE	rSCAN	HSE06	HF
Si	2.45	1.86	1.50	1.66	2.82	0.635	0.667	0.488	0.399	0.779
Diamond	1.66	1.32	1.01	1.48	1.96	0.536	0.420	0.241	0.153	0.615
GaAs	1.69	1.71	1.57	1.61	4.09	0.157	0.206	0.128	0.124	1.297
Ge	1.60	1.71	1.75	1.69	4.78	0.113	0.207	0.135	0.134	1.657
NaCl	2.14	0.78	0.59	0.70	1.20	0.438	0.222	0.170	0.124	0.237
BaTiO ₃	3.07	2.68	1.59	1.76	3.57	2.742	2.983	1.992	2.021	2.705
SrTiO ₃	3.10	2.67	1.54	1.79	3.28	3.017	3.313	2.151	2.139	2.466
MnO	2.16	2.70	1.78	—	—	0.978	1.295	1.499	—	—
Mean	2.23	1.93	1.42	1.53	3.10	1.077	1.164	0.850	0.728	1.394

Hamiltonian with local potential $v_s(\mathbf{r})$. Then, to obtain the FE, we approximate

$$\Delta E_{\text{DFA}}^{\text{NL}}[\rho_{\text{exact}}] \simeq \Delta E_{\text{DFA}}^{\text{NL}}[\rho_{\text{DFA}}], \quad (30)$$

and we conclude

$$\Delta E_{\text{FE}} \simeq \Delta E_{\text{DFA}}^{\text{NL}}[\rho_{\text{DFA}}] + E_{\text{DFA}}[\{\phi_i^{\text{KS}}[\rho_{\text{exact}}]\}] - E_{\text{exact}}[\rho_{\text{exact}}]. \quad (31)$$

We note that the nonlocality contribution $\Delta E_{\text{DFA}}^{\text{NL}}[\rho]$ vanishes for local/semilocal DFAs (LDA/PBE) but in general $\Delta E_{\text{DFA}}^{\text{NL}}[\rho] \leq 0$, because the minimum energy of a nonlocal DFA is attained for the GKS orbitals. For this reason, if one performs a GKS inversion instead of a KS inversion, as done, for instance, by Garrick *et al.* [82], there is no separate nonlocality contribution since $\Delta E_{\text{DFA}}^{\text{NL}} = 0$.

Similarly, the DE [Eq. (27)] can be written as

$$\Delta E_{\text{DE}} = \Delta E_{\text{DFA}}^{\text{NL}}[\rho_{\text{DFA}}] - \Delta E_{\text{DFA}}^{\text{NL}}[\rho_{\text{exact}}] + E_{\text{DFA}}[\{\phi_i^{\text{KS}}[\rho_{\text{DFA}}]\}] - E_{\text{DFA}}[\{\phi_i^{\text{KS}}[\rho_{\text{exact}}]\}]. \quad (32)$$

Using Eq. (30), we have

$$\Delta E_{\text{DE}} \simeq E_{\text{DFA}}[\{\phi_i^{\text{KS}}[\rho_{\text{DFA}}]\}] - E_{\text{DFA}}[\{\phi_i^{\text{KS}}[\rho_{\text{exact}}]\}]. \quad (33)$$

The calculated FEs and DEs for the DFAs considered in this work are given in Table III. For Si, diamond, and NaCl,

$\Delta E_{\text{FE}} > 0$ for all DFAs; for GaAs and Ge, it is negative for all DFAs except HF; and for MnO, it is negative for all DFAs considered. In BaTiO₃ and SrTiO₃, its sign depends on the DFA: it is positive for LDA and HF, but negative for PBE, rSCAN, and HSE06. Unlike the DE, there is no strict inequality for the FE [cf. Eqs. (26) and (27)].

In all the systems in our study, the DE was smaller in magnitude than the FE, in some cases by one to two orders of magnitude, with the notable exceptions of PBE and HSE06 for diamond, where the DE was larger in magnitude than the FE. This is unsurprising because most systems studied in this work are weakly correlated. Moreover, we found that rSCAN gave the lowest value of $|\Delta E_{\text{DE}}|$ across the systems studied, except for diamond and NaCl, where PBE had the lowest value, and Ge, where LDA had the lowest value. This is consistent with our findings that rSCAN had the smallest IAE and joint lowest $\mathcal{E}$. By contrast, the FE exhibited more variation; in the perovskites BaTiO₃ and SrTiO₃, HSE06 had the smallest functional error in magnitude, followed by LDA in BaTiO₃ but rSCAN in SrTiO₃. Outside these two perovskites, rSCAN was also the DFA with the smallest FE in magnitude, except in diamond, where PBE had the smallest FE, and in Ge and GaAs, where LDA had the smallest FE. It is, however, interesting to note that HSE06 often has lower total errors than rSCAN due to cancellation of DEs and FEs, notably in diamond.

TABLE III. DE and FE contributions to the total energy [see Eqs. (26) and (27)] of density functional approximations (DFAs) compared to QMC results. All energies are quoted in millihartrees (mHa) with errors indicated in round brackets. For nonlocal DFAs, the GKS orbitals were used to evaluate $E_{\text{DFA}}[\rho_{\text{DFA}}] = E_{\text{DFA}}[\{\phi_i^{\text{GKS}}[\rho]\}]$.

Material	LDA		PBE		rSCAN		HSE06		HF	
	FE	DE	FE	DE	FE	DE	FE	DE	FE	DE
Si	37.40(2)	−3.24(2)	26.10(2)	−3.03(2)	13.91(2)	−2.53(2)	30.68(2)	−8.76(2)	309.58(2)	−12.72(2)
Diamond	20.85(3)	−2.79(3)	0.94(3)	−2.17(3)	7.19(3)	−2.32(3)	58.95(3)	−59.12(3)	352.00(3)	−11.36(3)
GaAs	−24.46(3)	−1.20(3)	−40.29(3)	−1.23(3)	−52.51(3)	−1.11(3)	−30.60(3)	−9.34(3)	245.32(3)	−13.92(3)
Ge	−29.62(4)	−0.86(4)	−42.74(4)	−1.21(4)	−51.61(4)	−1.16(4)	−31.26(4)	−9.53(4)	253.52(4)	−15.70(4)
NaCl	89.71(2)	−2.58(2)	37.60(2)	−0.91(2)	5.44(2)	−0.94(2)	37.23(2)	−7.74(2)	275.28(2)	−3.60(2)
BaTiO ₃	65.1(3)	−46.5(3)	−137.0(3)	−48.0(3)	−107.0(3)	−29.5(3)	−56.4(3)	−39.8(3)	1035.9(3)	−62.4(3)
SrTiO ₃	95.6(3)	−51.3(3)	−100.7(3)	−52.5(3)	−73.9(3)	−32.0(3)	−21.3(3)	−42.9(3)	1066.6(3)	−56.2(3)
MnO	−1138.9(3)	−16.4(3)	−1430.1(3)	−20.6(3)	−802.2(3)	−12.6(3)	—	—	—	—

TABLE IV. GKS and KS gaps (in eV) for various DFAs. The KS gaps are obtained via inversion of the GKS density. The KS values for QMC are extrapolated to infinite system size (see Table I). In addition to the ('exact') KS gap obtained from inversion of the QMC density, the QMC fundamental gap E_g^{QMC} is listed where available. Mean absolute errors (MAEs) are quoted for each DFA relative to the QMC KS gap. Experimental (Expt.) values are taken from Ref. [38] unless otherwise stated.

	LDA	PBE	rSCAN		HSE06		HF		Quantum Monte Carlo		Expt.
	KS	KS	KS	GKS	KS	GKS	KS	GKS	KS	E_g^{QMC}	
Si	0.46	0.63	0.70	0.76	0.70	1.13	1.20	6.17	0.81	1.8(1) ^a , 1.50(2) ^b	1.17
Diamond	3.99	4.22	4.30	4.31	4.28	5.34	4.74	12.42	4.41	6.8(1) ^a , 5.94(4) ^c , 5.73 ^d	5.5
GaAs	1.16	1.38	1.46	1.60	1.46	1.94	1.96	7.07	1.37		1.52
Ge	0.26	0.43	0.49	0.56	0.51	0.88	1.03	5.73	0.38		0.79
NaCl	4.94	5.36	5.50	6.00	5.61	6.68	6.15	13.76	5.67		8.97
BaTiO ₃	1.81	2.24	2.56	2.66	2.78	3.46	4.77	11.73	3.21		3.2 ^e
SrTiO ₃	1.89	2.35	2.69	2.80	2.90	3.49	4.87	11.72	3.42		3.25 ^f
MnO	2.89	3.23	3.24	3.32	—	—	—	—	2.95	4.8(2) ^g	3.9 ^h
MAE	0.60	0.39	0.29		0.22		0.78				

^aUsing Slater-Jastrow (SJ) result from Ref. [95]

^bReference [96].

^cReference [97].

^dReference [98].

^eReference [99].

^fReference [100].

^gReference [101] using Ne core pseudopotentials.

^hReference [102].

Finally, it comes as no surprise that HF is the worst overall with regard to FE as the lack of correlation energy in the HF functional leads to FEs that are one to two orders of magnitude larger than those of standard DFAs. Nonetheless, it is noteworthy that in spite of this much larger FE, the DE for HF remains comparable to other DFAs.

V. BAND GAPS AND THE EXCHANGE-CORRELATION DERIVATIVE DISCONTINUITY

It is well known that the (exact) KS band gap $E_{g,s}$ is not equal to the fundamental gap E_g of the system, but rather

$$E_g = E_{g,s} + \Delta_{xc}, \quad (34)$$

where Δ_{xc} is the XC derivative-discontinuity [79,80,103–108].

The relative contributions of Δ_{xc} and $E_{g,s}$ to E_g in solids are generally unknown. In particular, it is believed that in strongly correlated systems dominated by Mott physics, $E_{g,s}$ is zero or negligible, such that the contribution to the fundamental gap E_g is largely from the exchange-correlation derivative discontinuity Δ_{xc} as discussed in Refs. [109–112].

Benchmarking the KS gap compared to other properties such as lattice parameters and cohesive energies is particularly challenging for similar reasons as the exact KS potential v_s , namely that it is not an experimental observable. Although inversion offers a potential approach to gauge the size of $E_{g,s}$, the gaps obtained are highly sensitive to the pseudopotentials used for the calculation, and particularly to the treatment of semicore states as (frozen) core states, as discussed in Appendix A.

In Table IV, we report both KS and GKS gaps for the systems considered in this work. Note that the KS gaps reported for the rSCAN, HSE, and HF functionals are obtained via inversion of the respective GKS target densities.

Formally, Δ_{xc} is defined through total-energy differences as the correction required to relate the KS eigenvalue gap to the fundamental gap. In finite systems, Δ_{xc} can also be interpreted as a constant shift of the local XC potential $v_{xc}(\mathbf{r})$ when the particle number crosses an integer [104–106]. This interpretation relies on the asymptotic decay of the KS orbitals and does not carry over to periodic solids. In GKS schemes, the nonlocal effective potential acts differently on occupied and unoccupied states (see Ref. [79]), thereby simulating the piecewise linear behavior of the total energy at integer N . Thus the difference between the GKS and KS gaps provides an estimate of the XC discontinuity.

That being said, although XC potentials $v_{xc}(\mathbf{r})$ of a nonlocal DFA, obtained via inversion of the DFA GKS density, are similar to the KS XC potentials obtained via OEP [57,58,61], the inverted XC potentials do not strictly have a Δ_{xc} , because the inverted potentials are not functional derivatives of an XC energy functional $E_{xc}[\rho]$. The same, of course, holds for the XC potentials obtained by inversion of the QMC density. Nonetheless, based on the similarity of the inverted XC potentials with OEP for a nonlocal DFA, we will loosely refer to the XC discontinuity of the inverted XC potentials.

First, we note that the KS gap obtained by inverting the DFA GKS density is always smaller than the GKS gap, because the nonlocal GKS operator already distinguishes between occupied and unoccupied orbitals and does not need an XC discontinuity to reproduce the piecewise linear change of the total energy with electron number, whereas the local KS potential does. The degree to which the GKS and KS gaps differ is a measure of the nonlocality of a given DFA within GKS, as discussed in greater detail in Ref. [61]. Among GKS methods, HF yields the largest gap, and it is unphysically large. This is attributed primarily to the lack of correlation (which overlocalizes HF densities), but also to the asymmetric action of the nonlocal Fock exchange operator on occupied

and unoccupied states, beyond the familiar distinction that occupied electrons are repelled by $N - 1$ electrons whereas unoccupied orbitals are repelled by N electrons. In a modified jellium model, Blair *et al.* [113] showed that this asymmetry can push the divergence in the jellium dispersion relation to arbitrarily high energies, leading to an excessive separation between artificially “occupied” and “unoccupied” states that is not directly related to physical screening. In most of the systems studied, the size of the KS gap tends to follow the progression of functionals in the “Jacob’s ladder of density functional approximations” [74], with LDA having the smallest gap, followed by PBE (GGA), rSCAN (meta-GGA), and HSE06 (hybrid DFA). The KS gap obtained by inverting the HF density is the largest. It exceeds the reference KS gap from the inverted QMC density, reflecting the overlocalization of the HF density caused by the lack of correlation.

Based on the systems studied, we further found that the mean absolute error of each DFA’s KS gap relative to the KS-QMC gap likewise follows the ascendancy of Jacob’s ladder, with KS-HSE06 having the lowest mean absolute error (MAE) of 0.22 eV and KS-rSCAN following closely behind with an MAE of 0.29 eV. However, we note that the KS gap from QMC is not always larger than the KS gaps of DFAs (besides HF-KS), particularly in MnO, where both the PBE gap and the KS-rSCAN gap are larger than the KS-QMC gap. Transition metals are well known within both DFT and QMC to be particularly sensitive to the treatment of the semicore states [101,114,115], and this is no different for Mn with the treatment of the $3s$ and $3p$ states as frozen core states.

For completeness, we remark that the DFA KS gaps for MnO change significantly when using the LDA pseudopotentials [116] of M.-H. Lee [117] instead of the TN Dirac-Fock pseudopotentials, despite both pseudopotentials treating the same electronic states as core states, differing only in the level of theory at which they are generated. For instance, the LDA KS gap changes from 2.89 eV with the TN pseudopotentials to 1.12 eV with the LDA pseudopotentials, the PBE KS gap changes from 3.23 to 1.71 eV, and the rSCAN KS gap changes from 3.24 to 1.87 eV.

In the case of nonlocal DFAs, an estimate of the derivative discontinuity Δ_{xc} (or Δ_x in the case of HF) is obtained from the difference between the GKS and KS values for each functional. In particular, we can see that although HSE06 and rSCAN have comparable performance with regard to the accuracy of the KS gap (relative to KS-QMC), the GKS-HSE06 gaps are larger than the GKS-rSCAN gaps. This is due to the use of the nonlocal Fock exchange operator in HSE06 (see also Refs. [79,80]). In Ref. [61], it was found that the GKS-HSE06 had a lower MAE relative to experimental results for a range of semiconductors and insulators (a subset of which we study in our present work); based on the results in this study, the higher accuracy of HSE06 appears to be due to the better estimate of Δ_{xc} in GKS rather than an improvement in the density or the XC potential $v_{xc}(\mathbf{r})$, at least in the systems studied.

It is also worth noting that the differences in KS gaps arise almost entirely from differences in $v_{xc}(\mathbf{r})$, since the differences in $v_H(\mathbf{r})$ were found to be relatively small.

The magnitude of the full Δ_{xc} itself could in principle be inferred by comparing the KS-QMC gaps to experimental

gaps. However, care should be taken when doing this due to pseudopotential effects as well as physical effects such as band gap renormalization due to electron-phonon interactions and phonon zero-point renormalization that are ignored in our calculations, especially for diamond [95,118,119]. An alternative approach is to compare with results from more accurate electronic structure methods, but this can present its own problems. For example, in QMC the presence of finite-size errors can amount to a considerable systematic error [96], and the treatment of such errors is crucial for the accurate calculation of gaps as shown by the spread of QMC (fundamental) gaps E_g^{QMC} in Table IV. The high cost of such calculations has likewise limited their use, with only a few QMC gaps being reported in the literature.

VI. CONCLUSIONS

We have performed density inversion of QMC densities and obtained accurate KS potentials $v_s(\mathbf{r})$ and, by extension, accurate XC potentials $v_{xc}(\mathbf{r})$ for several insulating solids given the pseudopotentials used in the calculations. The accuracy of the inverted KS potentials depends on the quality of the target QMC densities, including the accurate treatment of finite-size errors as well as uncontrolled errors resulting from the treatment of semicore states as frozen core states in the pseudopotentials.

The QMC densities and the KS potentials obtained therefrom via inversion serve as benchmarks with which to compare popular DFAs at each rung of Jacob’s ladder of functionals, namely the LDA, PBE (GGA), rSCAN (meta-GGA), HSE06 (hybrid DFA), as well as the HF approximation. For comparison, we have used two metrics, the IAE as defined in Eq. (20) and the energy $\mathcal{E}$ as defined in Eq. (21), in which the potential difference is weighted by the density difference.

For the systems we studied, we found that although the DFAs produce similar electron densities, the corresponding differences in the exchange-correlation potential $v_{xc}(\mathbf{r})$ can still be substantial. This is especially evident in the perovskite systems BaTiO₃ and SrTiO₃, where regions with only slightly higher QMC densities compared to the DFAs gave rise to deeper and more attractive $v_{xc}(\mathbf{r})$ potentials.

Furthermore, we find that the differences among the KS potentials $v_s(\mathbf{r})$ of the same system calculated using different methods stem primarily from variations in $v_{xc}(\mathbf{r})$, while the differences in the Hartree potential $v_H(\mathbf{r})$ are comparatively minor due to the overall similarity in electron densities across these methods. As a result, the discrepancies in the KS gap $E_{g,s}$, and likely in other properties as well, can be attributed specifically to changes in $v_{xc}(\mathbf{r})$. This occurs despite the fact that the overall variation in $v_s(\mathbf{r})$ remains small, since $v_{xc}(\mathbf{r})$, while relatively minor in magnitude, has a clearly significant contribution.

As expected, HF yields the highest IAE per electron among all DFAs, due to its tendency to overlocalize the electronic density as a result of neglecting electron correlation. However, according to the second metric $\mathcal{E}$ defined in Eq. (21), the LFX potential obtained from the inversion of the HF density turns out to perform reasonably well compared with other DFAs, even though it is still an exchange-only potential.

In addition to comparing the potential and the density, we assess the quality of the approximate XC energy functional

$E_{xc}[\rho]$ of each DFA by following the density functional error analysis of Burke and coworkers [32–35], noting that our analysis distinguishes between standard and generalized KS schemes. In a similar vein to the previous observations, we find that the performance of functionals with regard to the DE ΔE_{DE} and the FE ΔE_{FE} is not uniform; that is to say, functionals that have a lower FE ΔE_{FE} do not necessarily have a lower DE ΔE_{DE} as well.

We have also calculated the KS gaps $E_{g,s}^{DFA}$ for each DFA (as obtained via density inversion for nonlocal DFAs), and compared them against the corresponding KS gap $E_{g,s}$ from the inversion of the QMC density, which serves as an approximation to the “exact” $E_{g,s}$. This comparison provides another metric to assess the quality of the DFAs. For the rSCAN and HSE06 functionals, the KS gaps are similar to the KS-QMC gaps.

Finally, the improved accuracy of rSCAN and HSE06 in the calculation of the fundamental gap E_g is due to the approximate incorporation of the XC derivative discontinuity Δ_{xc} within the GKS calculation. The difference between the KS and GKS gaps for a given DFA is an estimate of the exchange and correlation derivative discontinuity Δ_{xc}^{DFA} for that DFA. In particular, for HF the difference between the LFX (KS-HF) gap and the HF gap gives the exchange discontinuity Δ_x .

In principle, the KS-QMC gaps could be compared to experimental gaps in order to infer the size of the XC discontinuity Δ_{xc} of the exact $v_{xc}(\mathbf{r})$ for these systems. However, this approach is prone to introducing systematic errors from the use of pseudopotentials in the KS-QMC gap and the neglect of other physical effects present in the fundamental gap E_g , such as the phonon corrections (zero-point renormalization, thermal phonon renormalization, electron-phonon coupling), which are known to be significant, e.g., in diamond.

In our present study, although inversion allows the overall XC contribution $v_{xc}(\mathbf{r})$ to be separated from $v_s(\mathbf{r})$, inversion algorithms themselves cannot be used to further isolate the individual exchange $v_x(\mathbf{r})$ and correlation $v_c(\mathbf{r})$ contributions. It has been noted from studies in finite systems, notably in the work of Bartlett and coworkers [120–125], that while the overall $v_x^{DFA}(\mathbf{r})$ and $v_{xc}^{DFA}(\mathbf{r})$ from various DFAs qualitatively reproduce the exact $v_x(\mathbf{r})$ and $v_{xc}(\mathbf{r})$, respectively, this is not true for the correlation potential. To the best of our knowledge, such studies in solids are limited and thus present an exciting avenue for further research and potentially guide the development of future DFAs.

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DATA AVAILABILITY

The data that support the findings of this article are available through the Durham University Research Data Repository [126].

TABLE V. LFX (KS-HF) band gaps calculated from the inversion of the HF density using CASTEP NCP19 pseudopotentials and CASINO TN pseudopotentials along with the valence electronic configurations used in the pseudopotentials. An underline indicates states that are treated as valence using NCP19 pseudopotentials but as part of a frozen core in the TN pseudopotentials.

Material	TN ^a	NCP19 ^b	Valence configuration
Si	1.20	1.17	Si - $3s^2 3p^2$
Diamond	4.74	4.75	C - $2s^2 2p^2$
GaAs ^c	1.96	0.93	Ga - $\underline{3d^{10}} 4s^2 4p^1$ As - $\underline{3d^{10}} 4s^2 4p^3$
Ge	1.03	0.46	Ge - $\underline{3d^{10}} 4s^2 4p^2$
NaCl	6.15	6.21	Na - $\underline{2s^2 2p^6} 3s^1$ Cl - $3s^2 3p^5$
BaTiO ₃	4.77	4.07	Ba - $5s^2 5p^6 6s^2$ Ti - $\underline{3s^2 3p^6} 4s^2 3d^2$ O - $2s^2 2p^4$
SrTiO ₃ ^d	4.87	4.25	Sr - $\underline{4s^2 4p^6} 5s^2$

^aThis work.

^bReference [61].

^cChanges from direct to indirect gap using TN pseudopotentials.

^dTi and O valence configurations are the same as BaTiO₃.

APPENDIX A: EFFECT OF TREATMENT OF SEMICORE STATES IN CALCULATED KS GAPS

For consistency, the same set of pseudopotentials is used for all calculations on a given system, fixing the external potential term in the KS Hamiltonian. Consequently, when comparing KS (XC) potentials obtained from the inversion of QMC densities with those from other DFAs, any differences arise from the functionals themselves rather than from variations in pseudopotentials, ensuring that each (pseudo)material is treated on an equal footing within each formalism.

However, the calculation of the KS gap can be highly sensitive to how semicore states are treated within the pseudopotential formalism, in particular whether they are treated as part of the (frozen) core or as valence. Since the TN pseudopotentials are obtained at the HF level of theory, to gauge the effect of the treatment of semicore states within the pseudopotential, we compared LFX band structures using the TN pseudopotential to those using CASTEP NCP19 on-the-fly-generated (OTFG) pseudopotentials (see Ref. [84]). The character of each band was determined via partial density of states (PDOS) calculations performed using the OptaDOS code [127], which implements the population analysis methodology of Segall *et al.* [128]. The adaptive broadening scheme of Yates *et al.* [129] was applied within the calculation of the PDOS. The resulting LFX band gaps are given in Table V along with the valence electronic configuration for the pseudopotentials.

In both Si and diamond, where the valence electronic configurations in TN and NCP19 pseudopotentials are identical, there is a negligible difference between the band gaps and indeed the band structures as shown in Fig. 10 for diamond,

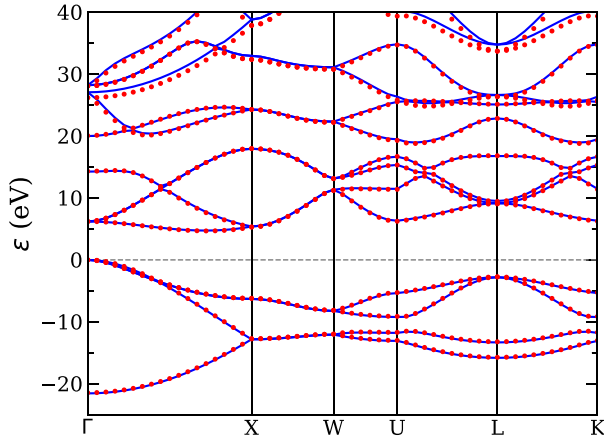


FIG. 10. Calculated LFX band structure of diamond using TN (blue, solid line) and NCP19 (red, dotted line) pseudopotentials. Note that the Fermi energy has been set to 0 eV.

although a larger deviation is obtained for higher unoccupied states that lie far away from the Fermi energy.

In NaCl, the Na 2s and 2p states can be considered as core states without significantly altering the results due to the large energy gap of over 10 eV between the lowest lying (Cl 3s) state and the Fermi level. The Na 2s and 2p states lie even further below the Cl 3s states as shown in Fig. 11, with the flat bands demonstrating the strong localization of these states that one might expect.

On the other hand, in GaAs, the Ga 3d states turn out to be semicore states and consequently their treatment in a frozen core can affect the calculated electronic structure, and in particular the calculated KS gap. This can be seen in both the band structures and PDOS in Fig. 12 for LFX calculations, where the 3d states are treated as valence by NCP19 pseudopotentials in Fig. 12(a) but as frozen core states by the TN pseudopotentials in Fig. 12(b). The LFX gap not only changes in value but also changes from direct to indirect, with a direct gap of 0.93 eV at the Γ point using NCP19 pseudopotentials becoming an indirect gap of 1.96 eV from $\Gamma \rightarrow X$ using TN pseudopotentials. The direct gap for the TN pseudopotentials is 2.43 eV. In addition to the gap, the actual dispersion of the individual bands is also altered. We find that for NCP19 and TN pseudopotentials the valence bandwidths are 3.19 and 2.77 eV, respectively, and the conduction bandwidths are 4.03 and 2.86 eV, respectively.

These results highlight the importance of accurately treating the semicore states, particularly when comparing with experimental results. We remind the reader that in our work, we use the same pseudopotential and lattice parameters across DFA and QMC calculations to maintain a consistent external potential. This allows us to draw meaningful conclusions from the comparison between the DFA and the benchmark QMC results.

APPENDIX B: NONLINEAR CORE CORRECTIONS FOR THE EXCHANGE-CORRELATION POTENTIAL

Within the pseudopotential formalism, the total electronic density $\rho_{\text{total}}(\mathbf{r})$ is partitioned into the core $\rho_{\text{core}}(\mathbf{r})$ and the

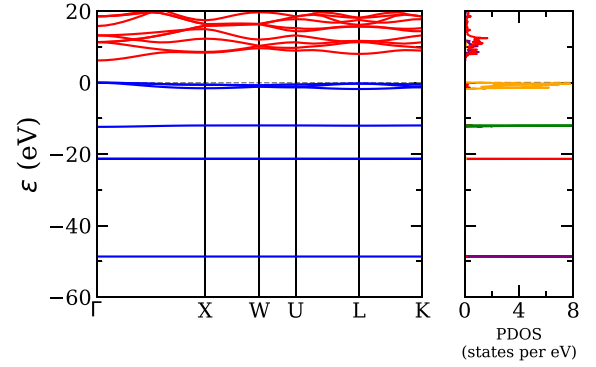


FIG. 11. Calculated LFX band structure and PDOS of NaCl using NCP19 pseudopotentials. Note that the Fermi energy has been set to 0 eV. Left: blue indicates occupied bands and red unoccupied; right: purple Na 2s, red Na 2p, green Cl 3s, and orange Cl 3p states.

valence $\rho_{\text{val}}(\mathbf{r})$ densities, the former of which is typically frozen in calculations. The pseudopotential is constructed by first performing an all-electron atomic calculation to obtain the “screened” potential $v_l^{\text{total}}(\mathbf{r})$ that is seen by the valence charge density in the atom $\rho_{\text{val}}^{\text{atom}}(\mathbf{r})$. The pseudopotential $v_l^{\text{ion}}(\mathbf{r})$ for the bare ion associated with the nuclear charge plus the core density contribution $\rho_{\text{core}}^{\text{atom}}(\mathbf{r})$ is then constructed by “unscreening” $v_l^{\text{total}}(\mathbf{r})$ by subtracting the Hartree and XC contributions associated with the valence charge density $v_{Hxc}[\rho_{\text{val}}](\mathbf{r})$ [130,131]:

$$v_l^{\text{ion}}(\mathbf{r}) = v_l^{\text{total}}(\mathbf{r}) - v_H[\rho_{\text{val}}](\mathbf{r}) - v_{xc}[\rho_{\text{val}}](\mathbf{r}). \quad (\text{B1})$$

As pointed out first by Louie *et al.* [131], there is an implied linearization in this procedure:

$$v_{Hxc}[\rho_{\text{total}}](\mathbf{r}) = v_{Hxc}[\rho_{\text{core}}](\mathbf{r}) + v_{Hxc}[\rho_{\text{val}}](\mathbf{r}), \quad (\text{B2})$$

where $v_{Hxc}[\rho](\mathbf{r}) = v_H[\rho](\mathbf{r}) + v_{xc}[\rho](\mathbf{r})$.

Although this is true for the Hartree potential, the XC potential is typically nonlinear in the density and thus simply replacing the total charge density with the pseudovalence density in a solid-state calculation can only be an approximation. In particular, the pseudopotential depends on the valence configuration $v_l^{\text{ion}}(\mathbf{r})$ used to generate it. This greatly hampers its transferability, especially when there is a significant overlap between $\rho_{\text{core}}(\mathbf{r})$ and $\rho_{\text{val}}(\mathbf{r})$. Fortunately, this can be corrected through the use of nonlinear core corrections (NLCCs), in which the following expression is used in place of Eq. (B1):

$$v_l^{\text{ion}}(\mathbf{r}) = v_l^{\text{total}}(\mathbf{r}) - v_H[\rho_{\text{val}}](\mathbf{r}) - v_{xc}[\rho_{\text{val}} + \rho_{\text{core}}](\mathbf{r}), \quad (\text{B3})$$

as discussed in Refs. [131,132].

In our work, we find that the omission of NLCCs in the pseudopotential affects the shape of the XC potential $v_{xc}(\mathbf{r})$, particularly near ions. To illustrate the effects of NLCCs, we performed calculations for bulk Si with the PBE functional using three sets of pseudopotentials:

(1) the TN Dirac-Fock pseudopotentials used for all calculations in this work,

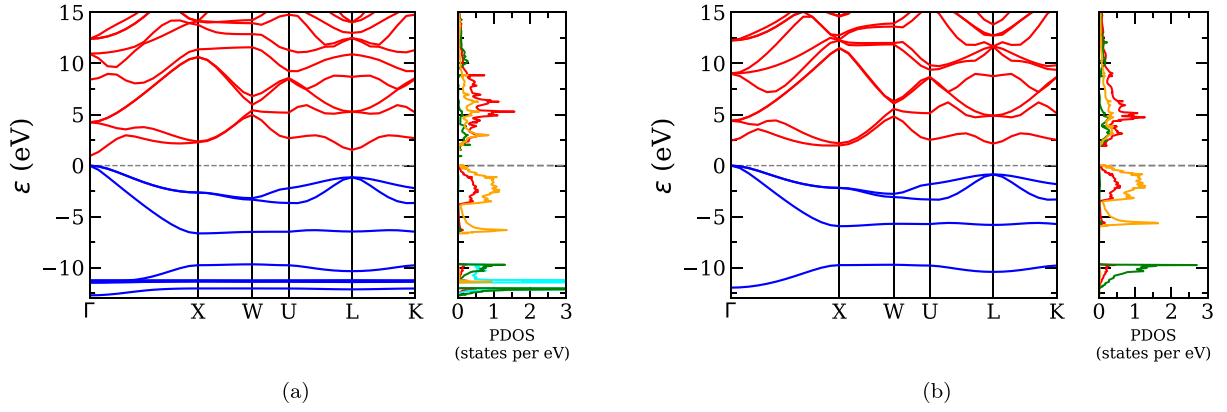


FIG. 12. Calculated LFX band structure and PDOS of GaAs using (a) NCP19 pseudopotentials and (b) TN pseudopotentials. Note that the Fermi energy has been set to 0 eV in each band structure. The color scheme for the band structure (left) is the same as that of Fig. 11. The color scheme for the PDOS (right) is as follows. Red: Ga 4p; cyan: Ga 3d; green: As 4s; and orange: As 4p. Note that the LFX gap changes from a direct gap at Γ with NCP19 pseudopotentials to an indirect gap at $\Gamma \rightarrow X$ with TN pseudopotentials.

(2) the norm-conserving pseudopotentials of M.-H. Lee [117], hereafter referred to as MHL [133],

(3) the OTFG pseudopotentials from the NCP19 library within CASTEP.

The TN and MHL pseudopotentials do not include NLCCs, while the NCP19 pseudopotentials do [84]. We further note that all these pseudopotentials use the same valence configuration as given in Table V. The results are shown in Fig. 13. The valence charge densities $\rho_{\text{val}}(\mathbf{r})$ of all three pseudopotentials are comparable, as expected since

they use the same valence configuration in their generation. However, the XC potentials for the TN and MHL pseudopotentials in Figs. 13(a) and 13(b) exhibit spikes near the nuclei that make the $v_{xc}^{\text{PBE}}(\mathbf{r}) > 0$ [where in reality, $v_{xc}^{\text{PBE}}(\mathbf{r}) \leq 0$]. The inclusion of NLCCs results in similar spikes, although they are now negative, as shown in Fig. 13. We note that away from ions, i.e., outside the core radius of the pseudopotential, $v_{xc}^{\text{PBE}}(\mathbf{r})$ is similar for the TN, MHL, and NCP19 pseudopotentials, since there is no contribution from $\rho_{\text{core}}(\mathbf{r})$.

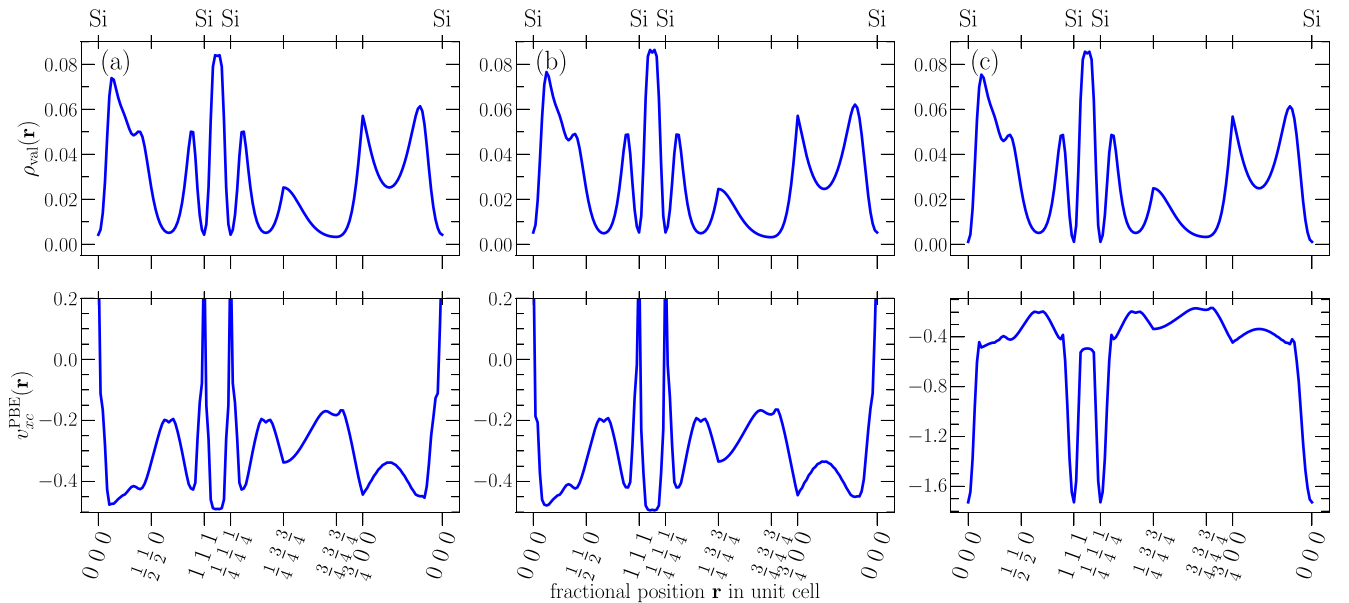


FIG. 13. Plot of the (valence) charge density $\rho_{\text{val}}(\mathbf{r})$ and the PBE XC potential $v_{xc}^{\text{PBE}}(\mathbf{r})$ in bulk Si for (a) TN pseudopotentials, (b) MHL pseudopotentials, neither of which include nonlinear core corrections (NLCCs), and (c) NCP19 on-the-fly-generated pseudopotentials in CASTEP (see main text) with NLCCs. $\rho_{\text{val}}(\mathbf{r})$ and $v_{xc}^{\text{PBE}}(\mathbf{r})$ are plotted along the path shown in Fig. 5(a). The valence configuration for all three pseudopotentials is identical (see Table V).

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