Foundations of the Ionization Potential Condition for Localized Electron Removal in Density Functional Theory

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Optimal tuning of functional parameters in density functional theory approximations, based on enforcing the ionization potential theorem, is a method of choice for the nonempirical prediction of the electronic structure of finite systems. This method has recently been extended to the bulk limit, based on an ansatz that generalizes the ionization potential theorem to the removal of an electron from a localized Wannier orbital. This Wannier-localization-based optimal tuning method has been shown to be highly successful for a wide range of periodic systems, accurately predicting electronic and optical properties. However, a rigorous theoretical justification for its foundational ansatz has been lacking. Here, we establish an ionization potential condition for the removal of an electron from a Wannier-localized orbital, by extending the piecewise linearity and Janak's theorems in density functional theory. We also provide numerical evidence supporting our theory.

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Density functional theory (DFT) has become the workhorse of first principles calculations across an unusually wide array of disciplines, as it offers predictive insights into many properties of molecules and solids, while offering an excellent balance between computational cost and accuracy [1–4]. However, DFT has historically struggled, often even qualitatively, in the description of electron and optical spectroscopy. Specifically, the band gap of semiconductors and insulators has been thought to be outside the reach of DFT even in principle, and the associated optical absorption spectrum outside the reach of time-dependent DFT with standard density functional approximations (DFAs) [5–8].

In molecules and other finite-sized objects, predictions of electronic and optical excitations have been found to be significantly improved [7,9–14] by forcing DFAs to obey an exact condition—the ionization potential (IP) theorem [15–18]. It states that for the exact functional, the IP from total energies difference is equal and opposite to the eigenvalue associated with the highest-occupied orbital of the (generalized) Kohn-Sham [(G)KS] [19,20] system. This relation is expressed as

$$E_{\text{g.s.}}^{N-1} - E_{\text{g.s.}}^{N} = -\epsilon_H, \tag{1}$$

where $E_{\text{g.s.}}^{N}$ and $E_{\text{g.s.}}^{N-1}$ are the ground-state (g.s.) energies of the N and $N-1$ electron systems, respectively, and ϵ_H is the highest-occupied eigenvalue of the (G)KS effective Hamiltonian. The IP theorem can be proven by combining the piecewise linearity (PWL) of the total energy in the fractional electron number between integer points [15,17,21] and Janak's theorem [22]. Importantly, Eq. (1) must be obeyed for exact (G)KS DFT, but is typically violated by DFAs [21,23].

Over the past two decades, many approaches have been developed to enforce the IP theorem (or a generalization thereof) in DFAs, in order to improve electronic structure predictions [9–14]. Here, as an important example we focus on optimal tuning (OT) [9] of (screened) range-separated hybrid [(S)RSH] functionals [24–27], where functional parameters are selected such that Eq. (1) is satisfied. This is because the exceptional accuracy of OT RSH in predicting electronic and optical excitations in molecules has been repeatedly demonstrated (see, e.g., Refs. [26,28–37]) and theoretically justified [38]. However, the argumentation is broadly applicable.

Unfortunately, it was recognized early on that in the bulk limit, *any* DFA exhibits PWL and thus trivially satisfies the IP theorem, regardless of accuracy (or lack thereof) in the resulting electronic structure [23,39–41]. As a result, the predictive power of IP-theorem-based approaches, including OT, is lost for periodic systems. This deficiency is a result of the delocalized nature of the (G)KS orbitals. A popular heuristic solution has been to instead work with localized-orbital-based approaches, giving rise to a wide range of broadly applicable methods to improve electronic structure predictions in the bulk limit within DFT (see, e.g., Refs. [12,13,42–53]). However, a rigorous theoretical justification of these approaches has been lacking—a critical gap that we remedy in this Letter by generalizing the IP theorem to address localized removal of an electron.

One particular approach that uses localized orbitals is the Wannier-localization-based optimal tuning (WOT) method [42], where the parameters of SRSH are selected based on enforcing an ansatz generalization of the IP theorem, inspired by the work of Ma and Wang [47]. This condition is expressed as

$$\tilde{E}^{N-1} - E^{N}_{\mathrm{g.s.}} = -\tilde{\epsilon}^{N}_{H}, \tag{2}$$

where $\tilde{E}^{N-1}$ is the total energy of an $(N-1)$-electron system under the constraint that the electron is removed from the Wannier orbital associated with the occupied manifold having the maximal expectation energy $\tilde{\epsilon}_H$ with respect to the GKS Hamiltonian of the N-electron system ($\tilde{\epsilon}_H$ is not an eigenvalue because the Wannier orbital is not an eigenfunction of the GKS Hamiltonian). WOT SRSH has proven to be highly accurate in predicting electronic and optical excitations for a wide range of periodic systems, both in itself and as a starting point for many-body perturbation theory calculations [42,54–61]. SRSH functionals using WOT-obtained parameters were then shown to yield excellent fundamental band gaps (from valence band maximum and conduction band minimum eigenvalues), optical absorption spectra (from linear-response time-dependent DFT), as well as surface and defect predictions [62,63]. We surmise that other properties—from dielectric response to magnetic moments—can also be addressed.

Given the success of WOT SRSH, an obvious question is *why* this approach yields such accurate results. However, to date, the WOT ansatz of Eq. (2) (or an approximate form of it) has not been derived from fundamental principles. In this Letter, we overcome this deficiency by validating the WOT ansatz from a theoretical standpoint, based on suitable extensions of the proof of the original IP theorem. Specifically, we provide a localized electron removal PWL condition and derive an exact generalized Janak's theorem, based on considerations involving unitarily transformed orbitals. The combination of these extensions gives rise to a generalized IP theorem for the removal of a localized electron, that explains the success of existing heuristic approaches and points the way to further developments. We further provide numerical evidence in support of the generalized PWL condition and its relation to the IP ansatz.

Our first step is to establish a generalized PWL condition for a *localized* quasihole state, noting that the density resulting from a local removal of an electron in an extended system does not correspond to the ground-state density of the $(N-1)$-electron system. To illustrate this important point, consider first the quasihole associated with the cation of a finite chain of M repeated units (e.g., as in an oligomer). In general, this quasihole is spread out over all M units and may be thought of as resulting from the removal of $1/M$ of an electron from each of M localized orbitals centered on each unit. If we assume that the localized frontier orbitals are energetically well separated from other orbitals, it follows that the lowest $M-1$ excited states of the chain cation also involve removal of $1/M$ electrons from the localized frontier orbitals, but with different phases on each unit. That is, the M lowest-lying eigenstates of the cation may be obtained from superpositions of localized states. The same analysis may, of course, be applied to any periodic system, where $M \to \infty$ in principle, but can be finite in practice if the localization is performed in a supercell.

Crucially, it follows from basic linear algebra that the localized states may equivalently be obtained by superpositions of the M eigenstates. Thus, rather than restricting to the usual ground-state analysis, we start our analysis by considering an *ensemble* [64–66] that mixes M ground and excited states—defined via an equally weighted ensemble density matrix (EDM) operator:

$$\hat{\Gamma}^{N-1}_{e} \equiv \frac{1}{M} \sum_{i=0}^{M-1} |\Psi^{N-1}_{i}\rangle\langle\Psi^{N-1}_{i}|. \tag{3}$$

Here, $\{|\Psi^{N-1}_{i}\rangle\}$ are eigenstates of the many-body Hamiltonian $\hat{H}$, the sum is over the subspace of the M lowest-energy eigenstates, and spin indices are suppressed throughout for simplicity. The ensemble energy and density are then given by

$$\mathcal{E}^{N-1}_{e} = \mathrm{Tr}\left[\hat{\Gamma}^{N-1}_{e}\hat{H}\right] = \frac{1}{M}\sum_{i=0}^{M-1} E^{N-1}_{i}, \tag{4}$$

$$n^{N-1}_{e} = \mathrm{Tr}\left[\hat{\Gamma}^{N-1}_{e}\hat{n}\right] = \frac{1}{M}\sum_{i=0}^{M-1} n^{N-1}_{i}, \tag{5}$$

respectively. Here, $E^{N-1}_{i} \equiv \langle\Psi^{N-1}_{i}|\hat{H}|\Psi^{N-1}_{i}\rangle$ and $n^{N-1}_{i} \equiv \langle\Psi^{N-1}_{i}|\hat{n}|\Psi^{N-1}_{i}\rangle$, where $\hat{n}$ is the density operator. Because it represents an equally weighted ensemble, the EDM in Eq. (3) remains invariant under a unitary transform of $\{|\Psi^{N-1}_{i}\rangle\}$. Thus, the set of wave functions,

$$|\tilde{\Psi}^{N-1}_{p}\rangle \equiv \sum_{i=0}^{M-1} \mathcal{U}_{ip}|\Psi^{N-1}_{i}\rangle, \tag{6}$$

for an arbitrary $M \times M$ unitary matrix $\mathcal{U}$, obeys

$$\hat{\Gamma}^{N-1}_{e} = \frac{1}{M}\sum_{p=0}^{M-1} |\tilde{\Psi}^{N-1}_{p}\rangle\langle\tilde{\Psi}^{N-1}_{p}|. \tag{7}$$

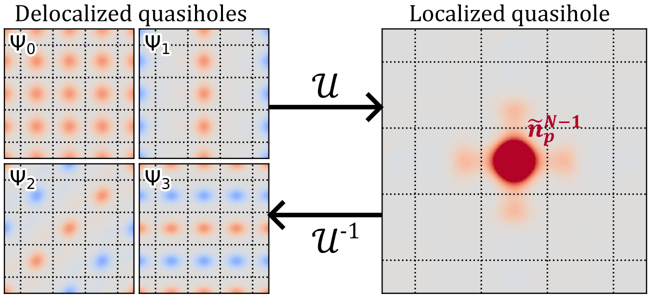

FIG. 1. Illustration of a system comprising repeating units, where many-body wave functions obtained by removal of delocalized quasiholes are transformed into a wave function obtained from the removal of a localized quasihole, with density $\tilde{n}_p^{N-1}$ centered at unit p.

That is, the ensemble can be described as a weighted sum of true eigenstates, or equivalently as a weighted sum of appropriate superpositions of eigenstates.

Our fundamental strategy for achieving our goal of overcoming the delocalization of the quasihole state is to seek a unitary transformation $\mathcal{U}$ that would define an alternate localized quasihole state. This transformation should be such that (a) the density of the quasihole associated with each state $|\tilde{\Psi}_p^{N-1}\rangle$, i.e., $n^N - \tilde{n}_p^{N-1}$, where $\tilde{n}_p^{N-1} \equiv \langle \tilde{\Psi}_p^{N-1}|\hat{n}|\tilde{\Psi}_p^{N-1}\rangle$, is well localized in the vicinity of some specific unit p, as illustrated in Fig. 1, and is similar, up to translation, to the hole density of any other unit p', and (b) the energies $\tilde{E}_p^{N-1} \equiv \langle \tilde{\Psi}_p^{N-1}|\hat{H}|\tilde{\Psi}_p^{N-1}\rangle$ are all degenerate and thus equal to the average ensemble energy, $\tilde{E}_p^{N-1} = \tilde{E}_{p'}^{N-1} = \cdots = \mathcal{E}_e^{N-1}$. The modest assumption behind satisfying both (a) and (b) follows from physical intuition based on nearsightedness [67] and practical experience in systems of repeating units; see Appendix A for details. Assumption (b), in fact, can always be satisfied; see Appendix B for a proof. The numerical results presented below further validate the assumptions.

The localized removal states $\{|\tilde{\Psi}_p^{N-1}\rangle\}$ describe a system where a localized electron removal from any of the M units is equivalent to removal from any of the other units (up to edge effects which we assume to be negligible, and do not occur in fully periodic systems). This construction can be thought of as the many-body analogy of removal of a maximally localized Wannier orbital [68], with the localized object being a quasihole in the many-body system, obtained from a unitary transformation over delocalized quasiholes, as illustrated in Fig. 1. In the case of the chain scenario discussed above, this is akin to applying the orbital-based argument to the M lowest-lying many-body wave functions. In larger or bulk systems it can be applied to a supercell of M units that is sufficiently large to represent the bulk of the $(N-1)$-electron system, and to allow for a state to be localized within it [69]. We emphasize that a repeating unit in our context is not necessarily confined to the smallest possible unit (namely, a primitive unit cell), but can be in itself composed of several primitive units.

Having introduced ensemble considerations, we now extend our analysis to the case of fractional number of electrons. We define the relevant $(N-q)$-electron system $(0 < q < 1)$ to be a fractional-charge ensemble [15], $\hat{\gamma}_f^{N-q} = (1-q)|\varphi^N\rangle\langle\varphi^N| + q\hat{\gamma}_e^{N-1}$, composed of an arbitrary N-electron state and an arbitrary $(N-1)$-electron excited-state ensemble, $\hat{\gamma}_e^{N-1}$, formed on M arbitrary orthonormal wave functions $\{\varphi^{N-1}\}$. The ground-state EDM is found by solving $\min_{\varphi^N,\{\varphi^{N-1}\}} \mathrm{Tr}[\hat{\gamma}_f^{N-q}\hat{H}] \equiv \mathrm{Tr}[\hat{\Gamma}_f^{N-q}\hat{H}]$, which, using standard ensemble argumentation [70,71], leads to

$$\hat{\Gamma}_f^{N-q} \equiv (1-q)|\Psi^N_{\mathrm{g.s.}}\rangle\langle\Psi^N_{\mathrm{g.s.}}| + q\hat{\Gamma}_e^{N-1}. \qquad (8)$$

This fractional electron EDM is composed of the unique N-electron ground state and the lowest M eigenstates of the $(N-1)$-electron Hamiltonian. It follows, using Eqs. (4) and (5), that

$$n_f^{N-q} = \mathrm{Tr}\left[\hat{\Gamma}_f^{N-q}\hat{n}\right] = (1-q)n^N_{\mathrm{g.s.}} + qn_e^{N-1}, \qquad (9)$$

$$\mathcal{E}_f^{N-q} = \mathrm{Tr}\left[\hat{\Gamma}_f^{N-q}\hat{H}\right] = (1-q)E^N_{\mathrm{g.s.}} + q\mathcal{E}_e^{N-1} \qquad (10)$$

are the density and energy, respectively, of the $(N-q)$-electron system. In light of the invariance of the excited-state EDM to a unitary transformation [Eq. (7)], Eqs. (9) and (10) are also left unchanged under it. However, by exploiting assumption (a) we obtain

$$\tilde{n}_p^{N-q} = (1-q)n^N_{\mathrm{g.s.}} + q\tilde{n}_p^{N-1}, \qquad (11)$$

for any $0 \leq p < M$, as a localized condition that is equivalent to Eq. (9). Likewise, assumption (b) yields

$$\mathcal{E}_f^{N-q} = (1-q)E^N_{\mathrm{g.s.}} + q\tilde{E}_p^{N-1}. \qquad (12)$$

Equations (11) and (12) thus constitute PWL conditions for the density and energy associated with localized electron removal from any of the units, and are the first major result of this Letter.

We now proceed to derive a generalized Janak's theorem. We start from the pure-state total energy functional, which in KS theory is written in the form [19]

$$E[n] = T_s[n] + E_{\mathrm{ext}}[n] + E_H[n] + E_{\mathrm{xc}}[n], \qquad (13)$$

where $T_s[n]$ is the kinetic energy of the noninteracting KS system, $E_{\mathrm{ext}}[n]$ is the energy due to the external potential, $E_H[n]$ is the Hartree energy, and $E_{\mathrm{xc}}[n]$ is the exchange-correlation energy. The KS equation is $H_{\mathrm{KS}}\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r})$, where ψ_i and ϵ_i are the KS orbitals and eigenvalues, respectively, and $H_{\mathrm{KS}} \equiv -\frac{1}{2}\nabla^2 + v_{\mathrm{ext}}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r})$, with the subscripts of the potential terms corresponding to those of the energy terms.

The density and kinetic energy of a fractionally occupied KS system, as defined by Janak [22], are $n(\boldsymbol{r}) = \sum_i f_i |\psi_i(\boldsymbol{r})|^2$ and $T_s = \sum_i f_i \langle\psi_i| -\frac{1}{2}\nabla^2|\psi_i\rangle$, where $\{f_i\}$ are occupation numbers between 0 and 1. Within these definitions, Janak's theorem states that

$$\frac{\partial E}{\partial f_i} = \epsilon_i. \tag{14}$$

Now consider a unitary transform of the KS orbitals,

$$|\tilde{\psi}_i\rangle = \sum_j U_{ji}|\psi_j\rangle, \tag{15}$$

where U_{ji} are the matrix elements of an arbitrary unitary matrix. The density and kinetic energy can then be expressed in terms of the unitarily transformed orbitals:

$$\begin{aligned} n(\boldsymbol{r}) &= \sum_j \sum_{j'} \tilde{f}_{jj'} \tilde{\psi}^*_{j'}(\boldsymbol{r}) \tilde{\psi}_j(\boldsymbol{r}), \\ T_s &= \sum_j \sum_{j'} \tilde{f}_{jj'} \langle\tilde{\psi}_{j'}| -\frac{1}{2}\nabla^2 |\tilde{\psi}_j\rangle, \end{aligned} \tag{16}$$

where the occupancy matrix elements $\tilde{f}_{jj'}$ are defined as

$$\tilde{f}_{jj'} \equiv \sum_i f_i U_{ij'} U^*_{ij}. \tag{17}$$

The trace of the occupancy matrix is invariant to the unitary transform, allowing for a (possibly fractional) number of electrons counted through summation over diagonal elements only, namely, $\sum_i f_i = \sum_j \tilde{f}_{jj}$ [72].

Next, consider the variation of the total energy with respect to one of the $\tilde{f}_{ii'}$ (and independent of the other occupancies), allowing for orbital relaxation. Using Eqs. (14) and (17), and noting that for the minimizing density $\frac{\delta E}{\delta\psi^*_j(\boldsymbol{r})} = \epsilon_j \psi_j(\boldsymbol{r})$ [22], we obtain

$$\begin{aligned} \frac{\partial E}{\partial \tilde{f}_{ii'}} &= \sum_j \frac{\partial E}{\partial f_j}\frac{\partial f_j}{\partial \tilde{f}_{ii'}} + \sum_j \int \frac{\delta E}{\delta \psi^*_j(\boldsymbol{r})}\frac{\partial \psi^*_j(\boldsymbol{r})}{\partial \tilde{f}_{ii'}} d^3r + \text{c.c.} \\ &= \tilde{\epsilon}_{ii'} + \sum_j \epsilon_j \frac{\partial}{\partial \tilde{f}_{ii'}}\left[\int \psi_j(\boldsymbol{r})\psi^*_j(\boldsymbol{r}) d^3r\right], \end{aligned} \tag{18}$$

where $\tilde{\epsilon}_{ii'} \equiv \langle\tilde{\psi}_{i'}|\hat{H}_{\mathrm{KS}}|\tilde{\psi}_i\rangle$. Because $\{\psi_j\}$ are normalized, the second term vanishes and we get

$$\frac{\partial E}{\partial \tilde{f}_{ii'}} = \tilde{\epsilon}_{ii'}. \tag{19}$$

Equation (19) is the second major result of this Letter. It is a generalized Janak's theorem, with Janak's original theorem being a special case thereof, where the unitary matrix is the identity matrix. Similar to Janak's theorem, no assumptions have been made about the exchange-correlation energy, implying that the result is applicable to both the exact functional and approximate ones. Importantly, an extension of the steps above to a hybrid functional only requires accounting for fractional occupancies in the exact-exchange energy; see Appendix C.

We can now use the above results to establish a generalized IP condition for the removal of a localized charge. As above, we make some physical assumptions about locality but otherwise use exact results. Consider a unitary matrix U for which there exists a subset $\{\tilde{\psi}_p\}$ in the N-electron system that is well localized on specific units such that their densities are all similar, up to translation, and reflect the quasihole densities obtained from $\mathcal{U}$ for the many-body system. In other words, we assume that $\mathcal{U}$ is the many-body equivalent of U, where in the many-body case $\mathcal{U}$ produces localized quasihole states and in the GKS case U produces a localized orbital. Consequently, the density of a system where one of the $\{\tilde{\psi}_p\}$ is fractionally occupied reflects the density of the system described by Eqs. (11) and (12). We now consider a variation in the total number of electrons by allowing a change only in the occupancy associated with the maximally occupied $\tilde{\epsilon}_{ii}$, $\tilde{f}_H \equiv 1 - q$ (recall that electrons are counted only through diagonal elements, $i = i' = H$). We then combine result (12) with result (19) to obtain

$$\tilde{E}^{N-1} - E^N_{\mathrm{g.s.}} = -\tilde{\epsilon}^N_H. \tag{20}$$

Equation (20) is the third major, and key, result of this Letter. It provides a rigorous justification of the IP ansatz of Eq. (2) via a significant generalization of the original IP theorem to the removal of an electron from a *Wannier-localized* orbital that is not an eigenstate of the GKS Hamiltonian. This provides a rigorous theoretical framework for optimal tuning in the thermodynamic limit, in which conventional optimal tuning is unhelpful [23]. We reiterate that the only formal assumptions made are (1) that, for the $(N-1)$-electron system, we can obtain M localized and nearly degenerate states from a unitary transform of the lowest M excited states, and (2) that there is a Wannier-like transformation of *noninteracting* (G)KS orbitals that can yield the localized hole densities of the *interacting* system. Within these modest assumptions, Eq. (20) is an exact result.

We now further discuss the link between the results presented above and the WOT strategy. Notably, the steps above apply to any choice of U and the Wannier transform is included within the set of possible unitary transforms described by Eq. (15). If U is the one associated with maximally localized Wannier orbitals, Eq. (20) reduces to the WOT ansatz. An intuitive, though informal, claim can be proposed as follows: the closer U is to the maximally localized unitary matrix, the greater the uniqueness and sensitivity achieved in bulk tuning. Conversely, the closer

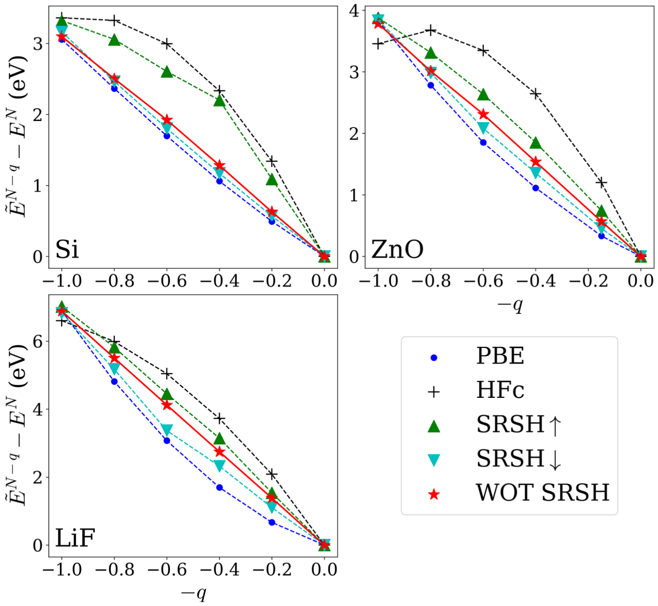

FIG. 2. Total energy as a function of the fraction of electron removed from the highest-energy Wannier orbital, for Si, ZnO, and LiF, computed using PBE, Hartree-Fock plus semilocal correlation (HFc), SRSH that overestimates (SRSH↑) or underestimates (SRSH↓) the band gap, and WOT SRSH.

U is to the identity matrix, the greater the nonuniqueness and insensitivity observed in bulk tuning. Furthermore, in a system of repeating units, maximally localized Wannier orbitals can be typically constructed such that there exists a subset that is localized on several of the different units with the same orbital nature and energy. Removal of an electron from each of these Wannier orbitals is then consistent with the theory.

To assess the reliability of our theory and justify its underlying assumptions, we turn to numerical results that demonstrate the PWL of WOT and its connection to the IP ansatz. To that end, we define a procedure for removing a fraction of an electron from the highest-energy Wannier orbital, based on constraining its occupancy and enforcing its orthogonality to the other orbitals self-consistently [73]. Further computational details are given in the Supplemental Material (SM) [74]. Using this procedure, we exploit fractional Wannier calculations, as shown in Fig. 2 and Table I, for Si, ZnO, and LiF. These materials were chosen to span a range of band gap values, from relatively narrow to very wide. The WOT SRSH parameters for these materials have been determined in prior work [42,56,84].

The PWL of $\tilde{E}$ with respect to q within WOT SRSH is clearly observed, as indicated by the small curvature [85], compared to the other DFAs which exhibit deviation from PWL. The very small remaining curvature is likely because the IP theorem and PWL are the same only to second order in the fractional charge within optimally tuned approximations—an issue previously observed within the context of the original IP theorem [38].

TABLE I. Fundamental band gap, E_g, determined from the difference between eigenvalues that correspond to the conduction band minimum and valence band maximum, and curvature, C, in eV, determined from a second-order polynomial fit of the curves in Fig. 2.

	Si		ZnO		LiF	
	E_g	C	E_g	C	E_g	C
PBE	0.6	0.6	0.8	1.8	9.1	4.4
HFc	6.0	−4.1	11.1	−5.3	21.6	−4.5
SRSH↑	3.6	−3.0	5.6	−1.3	17.9	−1.2
SRSH↓	1.0	0.4	2.2	0.8	12.9	2.3
WOT SRSH	1.2	−0.2	3.5	−0.1	15.3	0.0
Experiment[a]	1.2		3.8		15.3	

[a] See Appendix D for details.

We now focus on four other DFAs. First, the two limiting cases of the semilocal Perdew-Burke-Ernzerhof (PBE) functional [86] and Hartree-Fock plus PBE correlation (HFc) are considered. Second, we select non-optimally-tuned SRSH parameters such that the functional overestimates (SRSH↑) and underestimates (SRSH↓) the band gap (parameters are given in the SM [74]). These results demonstrate trends similar to those in unconstrained OT for small molecules [38,87]: the correct gaps (determined from eigenvalue differences between the conduction band minimum and valence band maximum in the neutral system) are associated with a PWL curve, underestimated gaps are associated with convex curves, and overestimated gaps are associated with concave curves. This analysis confirms that WOT SRSH successfully enforces PWL for localized electron removal. Furthermore, it establishes a clear connection between the functional's band gap prediction, its deviation from PWL, and its fulfillment of the IP ansatz, via the generalized Janak theorem. These observed trends across different DFAs, and the fact that the predicted gap is correct only when PWL against localized hole removal is obeyed, further support the validity of using PWL as a diagnostic for functional accuracy.

Three additional comments are in order. First, the principles underlying our theory extend beyond the WOT approach, and are relevant to aspects underlying other suggested methods that employ removal of localized charges [12,13,43,45–51]. Specifically, they allow for a meaningful connection to orbital-by-orbital correction-based approaches [88,89]: a link is found between PWL with respect to the occupancy of a unitarily transformed orbital and PWL in charge removal from deeper (G)KS orbitals. See the SM [74] for further discussion. Second, the present Letter used a specific ensemble DFT formalism to generalize the IP theorem and OT strategy to periodic systems. Recent work has explored IP-like relations for excited-state prediction [90–93]. This suggests that OT strategies could be extended to excited-state modeling, by combining recent developments in excited-state ensemble

DFT [94–97] and (W)OT theory. Third, a recent study [58] revealed that WOT and OT agree remarkably well also for molecules, even though the ground-state energy of the constrained and unconstrained ($N-1$)-electron systems differ significantly. This suggests that WOT can provide a generalized optimal tuning strategy beyond the solid-state limit.

To conclude, we have formulated a generalized IP condition, which relates the total energy difference upon removing an electron from a localized orbital, obtained from a unitary transformation, to its expectation value with respect to the (G)KS Hamiltonian. This result is exact under modest assumptions, and is founded on a generalized local removal PWL condition and a generalized localized-orbital-occupation-based Janak's theorem. The theory has been complemented by numerical evidence for the PWL of the total energy as a function of the fractional charge removed from the maximal-energy Wannier orbital. These insights lay a rigorous foundation for employing IP-theorem-based criteria involving localized orbitals, hitherto used without proof.

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Data availability—The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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[70] To show this result, first recognize that the N- and $(N-1)$-electron states may be minimized separately due to differing electron numbers. Then, the Hohenberg-Kohn principle yields $\varphi^N \to \Psi^N_{\text{g.s.}}$ and the Gross-Olivera-Kohn principle yields Eq. (3).

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End Matter

Appendix A: Physical arguments for localized charge removal—Our main proof of the localized IP theorem invoked a physically motivated assumption about "hole" localization. Key elements are discussed in the main text. Here, we add some further details to show that the physical assumptions are, in fact, quite modest.

Consider a cube of side length L of a crystalline material. For a sufficiently large L, the energy to remove a single electron will be essentially indistinguishable from the energy to remove a single electron from an infinite crystal. Thus, we may write $\mathrm{IP}_L = \mathrm{IP}$, where the equality indicates agreement in any practicable sense. Then, split the cube into eight smaller cubes of side length $L/2$. It follows that $\mathrm{IP}_{L/2} = \mathrm{IP}_L + \eta_{L/2} = \mathrm{IP} + \eta_{L/2}$, where $\eta_{L/2} \ll \mathrm{IP}$ is the change in energy associated with the smaller size. We may repeat this procedure to obtain $\mathrm{IP}_{L/2^p} = \mathrm{IP} + \sum_{q=1}^{p} \eta_{L/2^q} \equiv \mathrm{IP} + \zeta_p$, and terminate at some p^* when $\zeta_{p^*+1} \ll \mathrm{IP}$ is no longer satisfied.

We can now reassemble the original cube from the 8^p smaller cubes. The wave functions associated with removal from any smaller cube may be combined with the charge-neutral wave functions from all other cubes to form a wave function for the entire cube. The ionization potential associated with this wave function is $\mathrm{IP} + \zeta_{p^*}$ and its Fukui function (i.e., the density of its hole) is localized to the smaller cube, by construction. Note that here we have assumed that any artifacts from combining the wave functions of different cubes are small—a result that follows from the "nearsightedness" [67] assumption of typical electronic systems, applied to small cubes far away from the edge of the large cube. We may thus obtain degenerate wave functions, each confined to a cube of side length $L/2^{p^*}$ and each with an energy within $\zeta_{p^*} \ll \mathrm{IP}$ of the true IP. We may also, by symmetry, translate these wave functions along any integer combination of crystal lattice vectors to obtain localized states centered on any of the M crystal lattice points (up to the edge effects discussed above). Note that these wave functions are not necessarily eigenstates of any crystal Hamiltonian.

Furthermore, we can minimize edge effects by applying strict periodic boundary conditions to the cubes of various sizes, so that orbital-like and wave-function-like properties obey $\phi(x+P) = \phi(x)$, where $P = L/2^p$ is the appropriate periodicity. Then, the repeated division (or assembly) is equivalent to restricting (or loosening) the allowed periodicity of Bloch orbitals, which should obey $\phi_B(x+P) = e^{i\theta}\phi_B(x)$ in general. We note that similar reasoning may be used to justify the restriction to a finite $\boldsymbol{k}$ grid (rather than an integral) of Bloch orbitals in periodic DFT calculations. The mutual denominator of the $\boldsymbol{k}$ grid (on each dimension) represents the size (in crystal lattice units) of the subcrystal captured by the Bloch orbitals and thus, in practice, imposes a strict periodicity on the solution.

The key locality assumptions of the main text may thus be reframed as follows: (i) the smallest cube for which $\zeta_{p^*} \ll \mathrm{IP}$ is composed only of a small number of crystal lattice sites, so that the impact of edges is sufficiently small to be ignored (equivalent in practice to assuming that nearsightedness applies at a tens of Å scale), (ii) the energy required to remove an electron from an excited state of any $L/2^{p^*}$ cube is significantly greater than ζ_{p^*} so that the M local states are well separated in energy from higher states—we expand on this assumption below. It follows from these two assumptions that the wave functions for the smallest cubes form a complete basis for the lowest M eigenstates of the original cube, and vice versa. Using $\mathcal{U}_{pi}$ to indicate the transformation from the small cube basis to the full cube then yields

$$|\Psi_i^{N-1}\rangle \equiv \sum_{p=0}^{M-1} \mathcal{U}_{pi} |\tilde{\Psi}_p^{N-1}\rangle$$

$$\Rightarrow |\tilde{\Psi}_p^{N-1}\rangle \equiv \sum_{i=0}^{M-1} \mathcal{U}_{ip} |\Psi_i^{N-1}\rangle, \tag{A1}$$

where $\mathcal{U}_{ip} = \mathcal{U}_{pi}^*$ follows from the properties of unitary matrices. This relation justifies the results of the main text.

Before proceeding, we note that assumption (a) of the main text, namely, the localization of the many-body states, may be inapplicable in systems with small or zero band gap. The reason is that "excitations" of the lowest energy superpositions of cubes can potentially be lower in energy than the "ground states" of some of the higher energy superpositions of cubes. A similar issue can occur for insulators, where the problematic excitations involve several different "orbital levels"—i.e., a valence band. These "excited states" can intrude on the ensemble, and thus the localized superpositions can lose some of their good properties. However, in such cases it may be possible to form a basis of N_b eigenstates on each of the M lattice sites, by using the lowest N_b excitations of localized states. Here, N_b must be chosen to ensure that assumption (b) is obeyed collectively for the lowest N_b states (with appropriate adjustment to ζ_{p^*}). The theory results of the main text may then be obtained from the $M \times N_b$-state system with little modification. We note that materials like InSb and InAs, with a very small band gap, may fall under this extended definition, and that WOT works very effectively for these materials, as reported in Ref. [42].

Appendix B: Finding states with equal energies—Our central argument relies on a set of orthogonal states that (a) can be localized and (b) have the same energy as the ensemble. (a) relies on modest physical assumptions discussed in the previous appendix. (b) is equivalent to finding a unitary transformation Q of a diagonal matrix H (i.e., the matrix of the lowest M eigenstates of $\hat{H}$) that makes all diagonal elements of $H_Q = Q^T H Q$ the same (since the ensemble average is $M^{-1}\mathrm{Tr}[H] = M^{-1}\mathrm{Tr}[H_Q] = M^{-1}\sum_{i=0}^{M-1}[H_Q]_{ii}$). Conveniently, we can *always* find such a transformation.

Algorithmically this is done as follows. (1) Set $s = 0$ and $Q_{s=0} = I$ so that $H_{Q_0} = H$ is a diagonal matrix and compute $\tilde{E} = (1/M)\mathrm{Tr}[H]$. (2) Pick the index of the highest h and lowest l value entries on the diagonal of H_{Q_s} (at random if degenerate). Terminate and return H_{Q_s} if $|[H_{Q_s}]_{hh} - \tilde{E}| < \eta$ and $|[H_{Q_s}]_{ll} - \tilde{E}| < \eta$ for some infinitesimal η. (3) Define a rotation matrix R on h and l with angle (i) $\theta = \pm\sin^{-1}\sqrt{\{[(H_{Q_s})_{hh} - \tilde{E}]/[(H_{Q_s})_{hh} - (H_{Q_s})_{ll}]\}}$ if $|[H_{Q_s}]_{hh} - \tilde{E}| > |[H_{Q_s}]_{ll} - \tilde{E}|$, so that $[R^T H_{Q_s} R]_{hh} = \tilde{E}$, (ii) $\theta = \pm\sin^{-1}\sqrt{\{[\tilde{E} - (H_{Q_s})_{ll}]/[(H_{Q_s})_{hh} - (H_{Q_s})_{ll}]\}}$ otherwise, so that $[R^T H_{Q_s} R]_{ll} = \tilde{E}$ (the sign may be chosen at random). (4) Set $H_{Q_{s+1}} = R^T H_{Q_s} R$, $Q_{s+1} = Q_s R$, and $s \to s+1$ and repeat from step 2.

Note that selecting the extremes for h_s and l_s—where subscript s indicates that these indices change at each step—ensures that the unitary transformation is applied only once to each pair of terms. This is because one or the other term becomes equal to $\tilde{E}$, and thus cannot contribute to future iterations. Consequently, the off-diagonal elements $[H_{Q_s}]_{h_s l_s} = [H_{Q_s}]_{l_s h_s}$ (initially zero) become nonzero only *after* h_s or l_s is eliminated and so do not interfere with step 3. It follows from the invariance of the trace that $S \leq M$ repetitions must ensure that *all* diagonal elements are equal to $\tilde{E}$, since each step adds at least one additional $\tilde{E}$ to the diagonal.

This result reveals that assumption (b) is guaranteed provided M is finite and the spectrum of H is bounded above and below—conditions typically satisfied by physical systems. It is thus only its combination with assumption (a) that requires physical motivation.

Appendix C: Generalized Janak theorem for the case of a GKS Hamiltonian—Fractional occupations can be defined for the exact-exchange energy via

$$\begin{aligned} E_{\mathrm{x}} &= -\frac{1}{2}\sum_i \sum_j f_i f_j \int\int \psi_i^*(\boldsymbol{r})\psi_j(\boldsymbol{r}) \\ &\quad \times \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\psi_i(\boldsymbol{r}')\psi_j^*(\boldsymbol{r}')d^3r d^3r' \\ &= -\frac{1}{2}\sum_i \sum_{i'} \sum_j \sum_{j'} \tilde{f}_{ii'}\tilde{f}_{jj'} \int\int \tilde{\psi}_{i'}^*(\boldsymbol{r})\tilde{\psi}_j(\boldsymbol{r}) \\ &\quad \times \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\tilde{\psi}_i(\boldsymbol{r}')\tilde{\psi}_{j'}^*(\boldsymbol{r}')d^3r d^3r', \end{aligned} \tag{C1}$$

and similarly for RSH functionals by including, e.g., an error function within the integrals [26].

For pedagogical reasons, the KS case and the hybrid GKS case have been discussed above separately. The two cases, however, may be addressed simultaneously by defining a one-body reduced density matrix,

$$\begin{aligned} \rho(\boldsymbol{r},\boldsymbol{r}') &\equiv \sum_i f_i \psi_i^*(\boldsymbol{r}')\psi_i(\boldsymbol{r}) \\ &= \sum_j \sum_{j'} \tilde{f}_{jj'}\tilde{\psi}_{j'}^*(\boldsymbol{r}')\tilde{\psi}_j(\boldsymbol{r}), \end{aligned} \tag{C2}$$

in which case the total energy of Eq. (13) can be written as a unique functional of ρ. Then, $E_{\mathrm{xc}}[\rho]$ captures the usual mixture of exact and approximate exchange and correlation of a hybrid functional.

Appendix D: Details of experimental band gaps used in Table I—For Si, the band gap quoted is the sum of the experimental room temperature fundamental band gap (1.12 eV [98]) and the zero-point renormalization energy (0.06 eV [99]). For ZnO, the band gap is the sum of the experimental room temperature optical band gap (3.53 eV [100]), the exciton binding energy (0.06 eV [101,102]), and a vibrational renormalization energy (0.19 eV [103]). For LiF, the band gap is the sum of the experimental room temperature fundamental band gap (14.20 eV [104]) and the zero-point renormalization energy (1.15 eV [50,105]).