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# Single Excitation Energies Obtained from the Ensemble “HOMO-LUMO Gap”: Exact Results and Approximations

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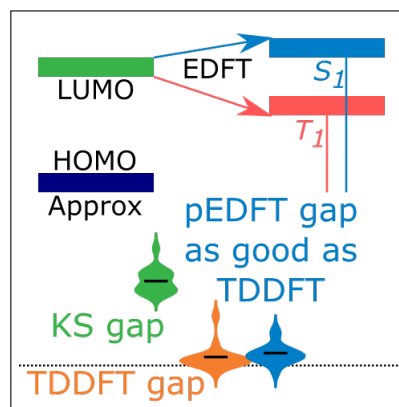
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## Abstract

In calculations based on density functional theory, the “HOMO-LUMO gap” (difference between the highest occupied and lowest unoccupied molecular orbital energies) is often used as a low-cost, *ad hoc* approximation for the lowest excitation energy. Here we show that a simple correction based on rigorous ensemble density functional theory makes the HOMO-LUMO gap exact in principle and significantly more accurate in practice. The introduced perturbative ensemble density functional theory approach predicts different and useful values for singlet–singlet and singlet–triplet excitations, using semi-local and hybrid approximations. Excitation energies are of similar quality to time-dependent density functional theory, especially at high fractions of exact exchange. The approach therefore offers an easy-to-implement and low-cost route to robust prediction of molecular excitation energies.

## TOC Graphic



Ground state calculations based on density functional theory<sup>1,2</sup> (DFT) have transformed chemical understanding and are increasingly used in a predictive fashion, owing to the availability of high quality density functional approximations (DFAs) that can be used at a relatively low computational cost.<sup>3-7</sup> The prediction of excited state properties is also of much importance and is usually addressed using time-dependent DFT (TDDFT).<sup>8-12</sup> Recently, ensemble DFT (EDFT)<sup>13,14</sup> is being increasingly explored<sup>15-31</sup> as a promising alternative to TDDFT for low-cost quantitative prediction of excitation energies.

Of particular importance is the lowest excitation energy, often referred to as the optical gap.<sup>9,32</sup> The DFT ‘‘HOMO-LUMO gap’’, defined as  $\epsilon_l - \epsilon_h$ , where  $\epsilon$  indicates an orbital energy,  $h$  indicates the highest occupied molecular orbital (HOMO), and  $l$  the lowest unoccupied molecular orbital (LUMO) is often used as a rough, computationally inexpensive approximation to the optical gap,<sup>9,32</sup> with some approximate argumentation<sup>33,34</sup> but no rigorous justification. In this work we first show that a carefully defined HOMO-LUMO gap within EDFT *exactly* yields the lowest lying excitation energy. Furthermore, this exact relation applies to both triplet and singlet excitations, and can be used with both traditional and hybrid density functional approximations (DFAs). We then show that using common DFAs, this relation leads to results of similar quality to those of TDDFT. The EDFT gap therefore is a low-cost, useful approach to the quantitative prediction of the lowest excitations.

We begin our considerations by briefly reviewing pertinent issues in DFT and EDFT. Conventional, pure state DFT<sup>1,2</sup> expresses the electronic ground state energy,  $E_0$ , as  $E_0 = \langle \Psi | \hat{H} | \Psi \rangle = T_s[n] + E_{\text{Hxc}}[n] + \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r}$ , where  $\Psi$  is the many-electron ground-state wave function,  $\hat{H}$  is the many-electron Hamiltonian,  $T_s$  is the non-interacting kinetic energy,  $E_{\text{Hxc}}$  is the Hartree-exchange-correlation (Hxc) energy,  $v$  is the external potential, and  $n$  is the electron density. The difficult many-body problem may then be replaced by the simpler problem of finding a set of one-body orbitals,  $\{\phi_i\}$

(elaborated below), from which one obtains the density,  $n = \sum_{i \in \text{occ}} |\phi_i|^2$ , as well as  $T_s$ . A DFA captures the requisite quantum mechanics by approximating  $E_{\text{Hxc}}$ .

EDFT for excited states<sup>13,14</sup> generalizes DFT to a statistical average across multiple states,  $\mathcal{E}^{\mathbf{w}} = \sum_{\kappa} w_{\kappa} \langle \Psi_{\kappa} | \hat{H} | \Psi_{\kappa} \rangle = \text{Tr}[\hat{\Gamma}^{\mathbf{w}} \hat{H}]$ , where  $\Psi_{\kappa}$  is the many-electron wave function associated with a specific energy level,  $\kappa$ ,  $w_{\kappa} \geq 0$  is the weight assigned to that energy level, and  $\hat{\Gamma} = \sum_{\kappa} w_{\kappa} |\Psi_{\kappa}\rangle \langle \Psi_{\kappa}|$  is an ensemble density matrix. Conventional DFT is then the special case  $w_0 = 1$  and  $w_{\kappa > 0} = 0$ . The relevant density is  $n^{\mathbf{w}} = \sum_{\kappa} w_{\kappa} \langle \Psi_{\kappa} | \hat{n} | \Psi_{\kappa} \rangle = \sum_i f_i^{\mathbf{w}} |\phi_i|^2$ , where  $f_i^{\mathbf{w}}$  are effective occupation factors that depend on the weights. Standard DFT machinery may be adapted to ensembles,<sup>13,14,19,21,22,24,25</sup> yielding  $\mathcal{E}^{\mathbf{w}} = \mathcal{T}_s^{\mathbf{w}}[n^{\mathbf{w}}] + \mathcal{E}_{\text{Hxc}}^{\mathbf{w}}[n^{\mathbf{w}}] + \int n^{\mathbf{w}}(\mathbf{r})v(\mathbf{r})d\mathbf{r}$  for a given ensemble state, and therefore  $\mathcal{E}^{\mathbf{w}} \approx \mathcal{T}_s^{\mathbf{w}}[n^{\mathbf{w}}] + \mathcal{E}_{\text{Hxc}}^{\text{EDFA},\mathbf{w}}[n^{\mathbf{w}}] + \int n^{\mathbf{w}}(\mathbf{r})v(\mathbf{r})d\mathbf{r}$  for an ensemble state obtained using a given DFA, where  $\mathcal{T}_s$  is the ensemble non-interacting kinetic energy and  $\mathcal{E}_{\text{Hxc}}$  is the ensemble Hxc energy. Excited state energies may then be computed via  $E_{\kappa} := \frac{\partial \mathcal{E}^{\mathbf{w}}}{\partial w_{\kappa}}$ , or other formulae.<sup>26,29</sup> EDFAs may thereby be used to predict properties of non-trivial excited states.

A typical practical DFT calculation involves finding orbitals,  $\phi_i$ , and orbital energies,  $\epsilon_i$ , obeying the (original<sup>2</sup> or generalized<sup>35</sup>/hybrid<sup>36</sup>) Kohn-Sham (KS or GKS) equation,  $\hat{h}\phi_i = \{\hat{h}_0 + \hat{v}_{\text{Hxc}}[n]\}\phi_i = \epsilon_i\phi_i$ . Here,  $\hat{h}_0 = -\frac{1}{2}\nabla^2 + v$  contains the one-body kinetic energy operator and nuclear potential,  $v$ . The Hxc potential,  $\hat{v}_{\text{Hxc}}[n]$ , maps the many-electron interactions to the one-body Hamiltonian. It may depend on spin (in an unrestricted Kohn-Sham formalism) and/or be non-multiplicative (in the GKS approach). All formalisms can be made exact, in the DFT sense of yielding the exact density and energy, for pure and degenerate ground states.<sup>2,25,35,37</sup> Moreover, in *any* exact calculation of a molecule, the HOMO eigenvalue,  $\epsilon_h$ , is the negative of the ionization potential (IP) of the system.<sup>37-41</sup> This relationship is often known as the ‘‘IP theorem’’.

In practice,  $\hat{v}_{\text{Hxc}} \approx \hat{v}_{\text{Hxc}}^{\text{DFA}}$  is obtained from a DFA and the resulting orbital energy,  $\epsilon_h^{\text{DFA}}$ , rarely comes close to satisfying the IP theo-

rem.<sup>42</sup> Kraisler and Kronik showed<sup>43–45</sup> that agreement between  $\epsilon_h^{\text{DFA}}$  and  $\text{IP}^{\text{DFA}}$  could be improved at essentially no cost by invoking exact relationships from ensembles with non-integer numbers of electrons.<sup>38</sup> This begs the question of whether similar improvements can be made to the HOMO-LUMO gap by means of excited-state ensembles.

In pioneering work, Levy<sup>46</sup> showed that excited state ensembles also obey an exact IP-like relationship – reproduced below as Eq. (1). However, the original derivation was only for the lowest excited state<sup>13,14</sup> and required the assessment of a generally unknown discontinuity in the functional derivative of the exchange-correlation energy. Here, we take advantage of recent advances in ensemble DFT<sup>23,25</sup> to develop a significantly broader approach that lends itself to approximations and can treat a wider class of excitations. Central to our approach is the use of ensemble GKS (EGKS) theory,<sup>25</sup> which yields orbitals obeying,  $\{\hat{h}_0 + \hat{v}_{\text{Hxc},i}^{\text{w}}[n]\}\phi_i^{\text{w}} = \epsilon_i^{\text{w}}\phi_i^{\text{w}} + \sum_{j \neq i} \epsilon_{ij}^{\text{w}}\phi_j^{\text{w}}$ , and which applies to both conventional and hybrid DFT. A crucial difference from conventional ground state DFT is that the effective potential  $\hat{v}_{\text{Hxc},i}^{\text{w}}$  can depend on the orbital label,  $i$  i.e., can be orbital specific; whereas ground state GKS theory involves a common (generally non-multiplicative) Hermitian operator for all orbitals. Orbital energies,  $\epsilon_i^{\text{w}}$ , have the same role as in ground states, but  $\epsilon_{i \neq j}^{\text{w}}$  are Lagrange multipliers to ensure orthogonality. EGKS for excited states can also be made exact, like its pure state counterpart.<sup>25</sup>

The EGKS framework is exact in the sense that each interacting state may be *mapped* to a non-interacting EGKS state involving the orbitals, while retaining the electron density of the original states. EGKS states are configuration state functions (CSFs),<sup>19,23,25</sup> i.e., sums of Slater determinants that account for fundamental symmetries. Each pure state or ensemble has a different set of orbitals. The CSFs capture complicated multi-reference characteristics of the interacting states because the orbitals provide an exact representation of the density<sup>19,25</sup> and properties thereof.

We illustrate our approach using the im-

portant case of excitations mapped to single promotion from a doubly occupied HOMO to the LUMO (of the ground state). The three CSFs of interest are then the ground state (gs)  $|S_0\rangle = |1^2 \dots h^2\rangle$ , and singly excited states (sx,  $h \rightarrow l$ )  $|T_1\rangle = |1^2 \dots h^\uparrow l^\uparrow\rangle$  and  $|S_1\rangle = \frac{1}{\sqrt{2}}[|1^2 \dots h^\uparrow l^\downarrow\rangle + |1^2 \dots h^\downarrow l^\uparrow\rangle]$ . Triplets are degenerate in EDFT<sup>19</sup> so we can equivalently choose one of the other two options. Our core theory then follows from three exact relationships:

1. The energy of the HOMO ( $h$ ) of the ground state ( $S_0$ ) GKS state is the ionisation potential of the interacting ground state system, i.e.,  $\epsilon_h^{S_0} = E_{\text{gs}}^{\text{int}} - E_{\text{gs}}^{\text{int}+}$ ,<sup>37–39,41,47,48</sup> where  $E_{\text{gs}}^{\text{int}}$  and  $E_{\text{gs}}^{\text{int}+}$  are the energy of the ground state of the system and its cation, respectively;
2. The energy of the highest occupied orbital of any singly-excited (sx  $\in \{T_1, S_1\}$ ) GKS state is given by  $\epsilon_l^{\text{sx}} = E_{\text{sx}}^{\text{int}} - E_{\text{gs}}^{\text{int}+}$ ,<sup>49</sup> where  $E_{\text{sx}}^{\text{int}}$  is the excited state energy and  $l$  indicates the ground state LUMO;
3. The energy of the highest occupied orbital of an EGKS system,  $\hat{\Gamma}^w = (1 - w)|S_0\rangle\langle S_0| + w|\text{sx}\rangle\langle \text{sx}|$  is equal to that of the sx,  $\epsilon_l^{\text{ens}} = \epsilon_l^{\text{sx}} = E_{\text{sx}}^{\text{int}} - E_{\text{gs}}^{\text{int}+}$ .

All three follow from fundamental relations between energy differences and the behaviour of electronic densities far from nuclei where a single orbital dominates.<sup>46,47,49</sup> Details are given in Section 1 of the Supporting Information (SI).

The consequence of the three relationships is that  $\Delta E_{\text{sx}}^{\text{int}} = E_{\text{sx}}^{\text{int}} - E_{\text{gs}}^{\text{int}} = \epsilon_l^{\text{ens}} - \epsilon_h^{S_0}$ , i.e., the excitation energy is *exactly* the difference between the eigenvalues of the ensemble orbital corresponding to the ground-state LUMO and to the ground state HOMO. For the family of ensembles,  $\hat{\Gamma}^{\text{sx},w} = (1 - w)|S_0\rangle\langle S_0| + w|\text{sx}\rangle\langle \text{sx}|$ , we may conveniently re-express this result as,

$$\Delta E_{\text{sx}}^{\text{int}} = \epsilon_l^{\text{sx},w} - \epsilon_h^{\text{sx},w=0}, \quad \forall 0 < w \leq \frac{1}{2}, \quad (1)$$

where the upper bound ensures that the low energy state is always weighted more than the excited state,<sup>13</sup> and we used that  $\hat{\Gamma}^{w=0} = |S_0\rangle\langle S_0|$

is a pure ground state. This is the same equation as Levy's Eq. (15),<sup>46</sup> but applies to GKS theory, and to low-lying excitations other than the absolute lowest. Finally, we may take the limit,  $w \rightarrow 0^+$ , of an infinitesimal excitation. As we show below, taking this limit in EGKS theory lets us bypass additional calculations<sup>25,26</sup> that would otherwise be necessary to compute the ensemble.

Eq. (1) is an exact result even in difficult excitations, despite similarities to recent, successful approximations.<sup>50</sup> It also applies more generally than the illustrative case of a singlet ground state. Firstly, it applies, as given, to systems where the triplet is the ground state and/or where  $\frac{1}{\sqrt{2}}[|1^2 \dots h^\uparrow l^\downarrow\rangle + |1^2 \dots h^\downarrow l^\uparrow\rangle]$  has a lower energy than  $|1^2 \dots h^2\rangle$ . Excitation energies simply become negative. Secondly, because the three exact relationships apply to the lowest excitation energy of any system, it may be adapted to ground states with large numbers of unpaired electrons, or spatial degeneracies.<sup>23</sup> In such cases one must identify the correct ensemble, as well as 'h' and 'l' to use in eq. (1). Section 1 of the SI justifies generalizations.

Let us now turn to approximations. A single excitation ( $S_0 \rightarrow T_1$  or  $S_0 \rightarrow S_1$ ) from  $h \rightarrow l$ , may be approximated by an ensemble DFA (EDFA),<sup>26,29</sup>

$$\mathcal{E}_{\text{Hxc}}^{\text{sx},w} \approx (1-w)E_{\text{Hxc}}^{\text{DFA}}[\rho_{S_0}] + wE_{\text{Hxc}}^{\text{DFA}}[\rho_{T_1}] + \Theta_{S_1} 2w \langle hl|lh \rangle, \quad (2)$$

Here,  $\rho_{S_0}$  is the one-body reduced density matrix (1-RDM) of  $|S_0\rangle$ , and  $\rho_{T_1}$  is the 1-RDM of  $|T_1\rangle$ . The DFA may be of conventional (e.g. PBE<sup>51</sup>), hybrid (e.g. B3LYP<sup>52</sup>) or range-separated hybrid (e.g.  $\omega$ B97x<sup>53</sup>) form, although the latter is not considered further. The last term in eq. (2) is the singlet-triplet splitting,  $2 \langle hl|lh \rangle = 2 \int \frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|} \phi_h(\mathbf{r})\phi_l^*(\mathbf{r}')\phi_l(\mathbf{r})\phi_h^*(\mathbf{r}')$ .  $\Theta_{S_1}$  indicates that it appears only if one is interested in  $S_0 \rightarrow S_1$ .

The energy is minimized by orbitals obey-

ing,<sup>25</sup>

$$[\hat{h}_0 + \hat{v}_{\text{Hxc},i}^{\text{sx},w}] \phi_i^{\text{sx},w} = \epsilon_i^{\text{sx},w} \phi_i^{\text{sx},w} + \sum_{j \neq i} \epsilon_{ij}^{\text{sx},w} \phi_j^{\text{sx},w}, \quad (3)$$

where  $\hat{v}_{\text{Hxc},i}^{\text{sx},w} \phi_i = \frac{1}{f_i^w} \frac{\delta \mathcal{E}_{\text{Hxc}}^{\text{sx},w}}{\delta \phi_i^*}$  are the EGKS potentials. Here,  $f_{i < h} = 2$ ,  $f_h = 2 - w$  and  $f_l = w$  are average occupation factors. The terms  $\epsilon_{ij}$  are required to preserve orthogonality. We may, without loss of generality, assume all quantities are real.

As a first step toward a useful approach, consider the potentials,  $\hat{v}_{\text{Hxc},i}$ , in the limit  $w \rightarrow 0^+$ . For all orbitals ( $i \leq h$ ) occupied in  $S_0$  we obtain,

$$\hat{v}_{\text{Hxc},i}^{\text{sx}} \phi_i^{\text{sx}} = \hat{v}_{\text{Hxc}}[\rho_{S_0}] \phi_i^{\text{sx}} + O(w), \quad \forall i \leq h, \quad (4)$$

where  $\hat{v}_{\text{Hxc}} := \frac{\delta E_{\text{Hxc}}^{\text{DFA}}[\rho_{S_0}]}{\delta \rho_{S_0}}$ . We use sx without explicit dependence on  $w$  to denote  $w \rightarrow 0^+$ . However, the LUMO,  $\phi_l$ , has a different effective potential. Only the  $O(w)$  terms of eq. (2) depend on  $\phi_l^*$ , meaning that  $\frac{\delta \mathcal{E}_{\text{Hxc}}^{\text{sx}}}{\delta \phi_l^*} = w \{ \hat{v}_{\text{Hxc}}^{\text{DFA}}[\rho_{T_1}] + \Theta_{S_1} 2\hat{v}_x[\rho_h] \} \phi_l$  where  $\hat{v}_{\text{Hxc}} := \frac{\delta E_{\text{Hxc}}[\rho_{T_1}]}{\delta \rho_{T_1,\uparrow}}$  is the majority spin potential, and  $\hat{v}_x$  is an exchange operator. But because  $f_l = w$  we obtain,

$$\hat{v}_{\text{Hxc},l}^{\text{sx}} \phi_l^{\text{sx}} = \{ \hat{v}_{\text{Hxc}}[\rho_{T_1}] + \Theta_{S_1} 2\hat{v}_x[\rho_h] \} \phi_l^{\text{sx}} + O(w). \quad (5)$$

Therefore,  $[\hat{h}_0 + \hat{v}_{\text{Hxc}}[\rho_{S_0}]] \phi_{i \leq h}^{\text{sx}} = \epsilon_i^{\text{sx}} \phi_i^{\text{sx}} + \epsilon_{il}^{\text{sx}} \phi_l^{\text{sx}}$ , and,  $[\hat{h}_0 + \hat{v}_{\text{Hxc},l}^{\text{sx}}] \phi_l^{\text{sx}} = \epsilon_l^{\text{sx}} \phi_l^{\text{sx}} + \sum_{i \leq h} \epsilon_{il}^{\text{sx}} \phi_i^{\text{sx}}$ . Details are in Section 2 of the SI.

Our next step is to make the reasonable<sup>37</sup> assumption that the orbitals,  $\phi_{i \leq h}$ , change only at  $O(w)$ . This means that the off-diagonal elements of  $\epsilon_{ij}^{\text{sx}}$  must also be  $O(w)$  and may be dropped. Consequently, the occupied ( $i \leq h$ ) orbitals obey the *same effective Hamiltonian* as a typical ground state calculation, i.e.,

$$\{ \hat{h}_0 + \hat{v}_{\text{Hxc}}^{S_0} \} \phi_i^{S_0} = \epsilon_i^{S_0} \phi_i^{S_0}, \quad \hat{v}_{\text{Hxc}}^{S_0} := \hat{v}_{\text{Hxc}}[\rho_{S_0}]. \quad (6)$$

To determine the LUMO,  $\phi_l^{\text{sx}}$ , we first expand

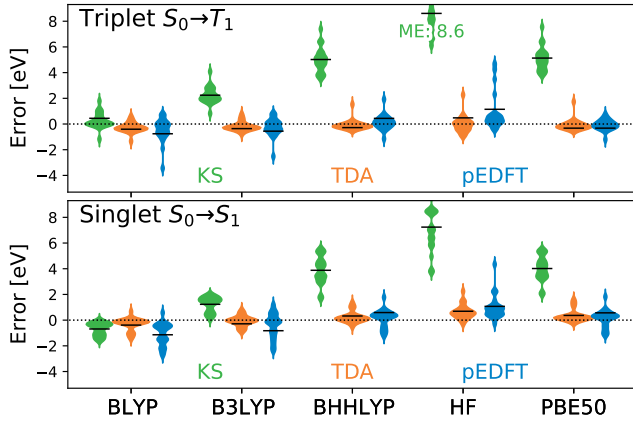


Figure 1: Violin plots showing the distribution of errors across triplet (top) and singlet (bottom) excitations from our test set. Excitations are obtained from KS DFT (green), TDA (orange) and the pEDFT (blue), using a variety of hybrid DFAs. Horizontal bars indicate the mean absolute error, shown as positive numbers when the mean error is positive, and negative otherwise.

it in terms of virtual orbitals,  $a > h$  only, giving  $\phi_l^{\text{sx}} = \sum_{a>h} U_{al}^{\text{sx}} \phi_a^{S_0}$ . This ensures it is orthogonal to all occupied orbitals. The eigenvalue equation,

$$\{\epsilon_a^{S_0} \delta_{ab} + [\Delta v_l]_{ab}^{\text{sx}}\} U_{bl}^{\text{sx}} = \epsilon_l^{\text{sx}} U_{al}^{\text{sx}}, \quad (7)$$

lets us determine  $U_{al}^{\text{sx}}$  and  $\epsilon_l^{\text{sx}}$ , where

$$[\Delta v_l]_{ab}^{T_1} = \int \phi_a^{S_0*} \{ \hat{v}_{\text{Hxc}}^{T_1}[\rho_{T_1}] - \hat{v}_{\text{Hxc}}^{S_0}[\rho_{S_0}] \} \phi_b^{S_0} d\mathbf{r}, \quad (8)$$

and  $[\Delta v_l]_{ab}^{S_1} = [\Delta v_l]_{ab}^{T_1} + 2\langle ha|bh \rangle$ . It is important to recognise that the appearance of  $\rho_{T_1}$  in eq. (8) means that eq. (7) must be solved self-consistently, because  $\rho_{T_1}$  depends on  $\phi_l$  which depends on  $U_{al}^{\text{sx}}$ . Procedurally, one: i) obtains orbitals and energies for  $i \leq h$  from a typical ground state singlet calculation; and ii) afterward obtains  $\epsilon_l^{\text{sx}}$  by iterating eqs. (7) and (8) to self-consistency – see Section 3 of the SI.

Finally, we see the excitation energy is given by,

$$\Delta E_{S_0 \rightarrow T_1 \text{ or } S_1} = \epsilon_l^{T_1 \text{ or } S_1} - \epsilon_h^{S_0}, \quad (9)$$

which we denote “perturbative EDFT”

(pEDFT) to stress that is obtained in the perturbative limit,  $w \rightarrow 0^+$ . The pEDFT HOMO-LUMO gap of eq. (9) would be exact if one had access to the exact Hxc functional. As shown below, it offers significant improvements on the regular HOMO-LUMO gap when conventional and hybrid DFAs are employed.

To assess the accuracy of pEDFT we calculate the the lowest lying  $S_0 \rightarrow T_1$  and  $S_0 \rightarrow S_1$  transitions from a 2018 benchmark set,<sup>55</sup> as well as the BeO ground state potential energy surface (PES). These examples are chosen due to their difficulty in possessing multiple low lying excited states, or in the case of BeO in reordering of the excited states across the PES. This is to demonstrate that pEDFT can perform well even in typically difficult systems, where other excitation calculation approaches might fail. For comparison we also calculate these transitions using KS orbitals and the Tamm-Dancoff approximation (TDA)<sup>56,57</sup> to time-dependent density functional theory (TDDFT). TDA and other TDDFT results are computed using ORCA.<sup>58</sup> Technical details are given in Section 4 of SI.

We pay specific attention to the symmetries of the electronic transitions calculated. Section 4 in the SI provides details of the orbitals that give rise to specific transitions, discusses the transition symmetry, and provides an accompanying discussion. We note that acquiring the correct transition symmetry, corresponding to the lowest energy excitation, is sometimes not strictly from the HOMO-LUMO gap, for example from HOMO to LUMO+2 instead. Transitions between the highest and lowest orbital of given symmetries obey a generalization of eq. (1), per the paragraph between Eqs (1) and (2). It is beyond the scope of the present work to resolve whether all such cases have a completely rigorous grounding. In the spirit of practicality we therefore take them as given in the remaining discussion.

First, we consider the benchmark set of Loos et al,<sup>55</sup> with 18  $S_0 \rightarrow S_1$  transitions and 17  $S_0 \rightarrow T_1$  transitions. To demonstrate that pEDFT can effectively utilize established DFAs we present results for a variety of hybrid DFAs with different fractions of exact ex-

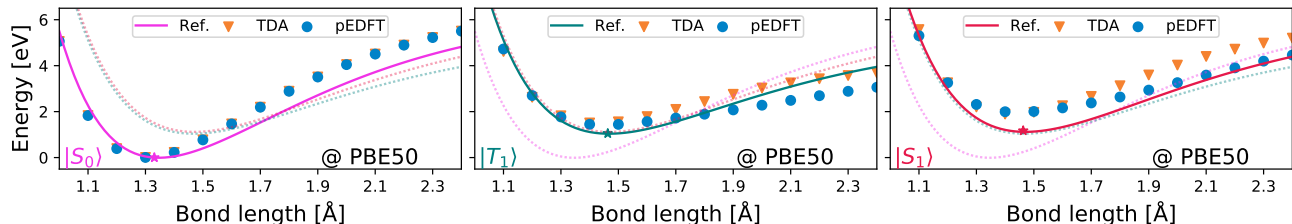


Figure 2: PBE50 potential energy surfaces for low-lying states of BeO, computed using TDA (orange triangles) and pEDFT (blue circles). Reference data is shown as solid lines (theory) and stars (experiment<sup>54</sup>). Zero is the optimized  $|S_0\rangle$  energy. Pale, dotted curves show other energy surfaces to reveal where level crossing occurs.

change: BLYP<sup>59</sup> (0%), B3LYP<sup>52</sup> (20%), BHHLYP<sup>60</sup> (50%), Hartree-Fock (HF, 100%) and PBE50 (50% HF in PBE0). The collective errors of these transitions for each method are presented in Figure 1 as violin plots, where widths indicate the probability of a given error. All calculations on the benchmark set are performed using aug-cc-pvtz<sup>61</sup> basis set.

The primary result from Figure 1 is the similar performance of pEDFT and TDA methods across the spectrum of fractional exact exchange. This comparison validates the accuracy of pEDFT as competitive with TDA (albeit with worse outliers). Additional analysis in Section 4.1 of SI reveals that pEDFT is similarly competitive with conventional TDDFT.

The secondary result is that gap opening by HF exchange<sup>32</sup> is completely cancelled by pEDFT, which validates the approach in hybrid theories. Indeed, results with 50% mixing seem to be optimal. This reflects the fact that the effective potential felt by unoccupied orbitals is corrected within the self-consistency cycle, which ensures that all orbitals are correctly bound.

So far we have focused on fixed geometries. To go beyond this restriction, the PES for BeO is presented in Figure 2, using pEDFT and TDA with PBE50 and aug-cc-pvtz. Excited state surfaces in BeO have been the subject of long-standing computational interest as a difficult case.<sup>62</sup> High-quality reference data is produced using MRCC.<sup>63</sup> Details are in Section 4.2 of SI.

Similar performance between pEDFT and TDA is again observed, particularly the prediction of the Morse potential minima of  $T_1$  and

$S_1$ , which are both slightly overestimated. The Morse potential curve of pEDFT is flatter than TDA. Both methods maintain a smooth curve through the rearrangement of excited states, which is a reflection of the stability of both methods, something not many excited state transition calculation approaches can boast, including spin-flip TDA.<sup>64,65</sup> Additional results (B3LYP, TDDFT and spin-flip TDA) are presented in Supplementary Figures 3–5.

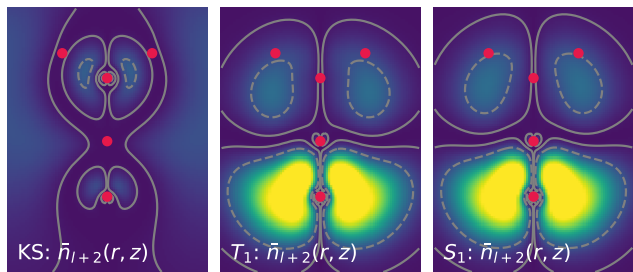


Figure 3: Densities,  $\bar{n}_{l+2} \propto \phi_{l+2}^2$ , of LUMO+2 orbitals in ketene averaged around the C-C-O axis. Reports the original KS orbital, (left) as well as orbitals after triplet ( $T_1$ , centre) and singlet ( $S_1$ , right) pEDFT self-consistency cycles – all for PBE. Solid/dashed lines are  $10^{-3}/10^{-2}$  contours.

Finally, let us consider the importance of the pEDFT self-consistency cycle that relaxes the “LUMO” to minimize the excitation energy. All of the excitations reported so far involve transitions between different spatial symmetries, meaning their orbitals change only a little during the pEDFT optimization as they are “preserved” by the symmetry. However, for the case of ketene using PBE in aug-cc-pvtz the HOMO and LUMO+2 orbitals have the same

fundamental symmetry (unlike  $h$  and  $l$ , used in the benchmark set) and therefore offer more interesting illustrative results. Figure 3 shows densities of the  $l + 2$  orbital, averaged around the C-C-O axis. The pEDFT cycle dramatically changes the density, whether used to compute  $T_1$  or  $S_1$ . Less obviously, the singlet and triplet densities are also different – charge moves toward the H atoms in the singlet. Technical details are in Section 4.3 of SI.

To conclude, we have shown that the “HOMO-LUMO” gap (and generalizations based on symmetries) can be made *exactly equal* to the excitation energy, by defining it carefully in terms of ensemble density functionals. By taking the limit of infinitesimal interactions it is possible to solve for the gap using a self-consistent cycle only on the LUMO. The resulting energy, Eq. (9), is rather effective when approximated: it improves conventional HOMO-LUMO gaps significantly, yields similar energies to TDA and TDDFT, and is able to describe the potential energy of BeO as well as TDA does, and better than spin-flip TDA.

Implementation of pEDFT relies only on existing DFA routines, and basic linear algebra operations. Thus, the pEDFT approach may be readily implemented in any quantum chemistry code. The implementation used for the present work is based on `Psi4`<sup>66</sup> and `numpy/scipy` and is available on `github`. Details are given in Section 5 of the SI.

There still remains scope for further improvement. Mostly, the pEDFT gap is of similar quality to its TDA or TDDFT counterpart, but there are a few cases (e.g. water) where its quality can be significantly worse. This may be partially explained by a failure to include density-driven correlations<sup>21,22</sup> in Eq. (2), leading to density-driven correlation errors in the resulting energy. Improvements may be possible by devising simple functionals for the density-driven correlation energy. Exploring why Chan and Hirao’s<sup>50</sup> orbital-energy-based technique improves excitation energies, and making connections to extended Koopman’s theorems,<sup>67–69</sup> may offer insights in this regard. This problem remains the topic of ongoing work.

Finally, we did not discuss forces here. How-

ever, we note that both  $\epsilon_h^{S_0}$  and  $\epsilon_l^{S_x}$  are obtained by variational formulae. Therefore, both should be amenable to Hellmann-Feynman treatment of forces, with the necessary adjustments for basis set incompleteness. We are presently working on implementing forces.

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## Supporting Information Available

Includes:

1. Details and generalizations of eq. 1 of the main paper
2. Details of pEDFT derivation
3. Pseudo-code implementation of pEDFT
4. Technical details of calculations, including supplementary figures and tables
5. Description of software

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