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Approximating Quasiparticle and Excitation Energies from Ground State Generalized Kohn-Sham Calculations

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3 December 25, 2018
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6 **Abstract**

7 Quasiparticle energies and fundamental band gaps in particular are critical prop-
8 erties of molecules and materials. It was rigorously established that the generalized
9 Kohn-Sham HOMO and LUMO orbital energies are the chemical potentials of electron
10 removal and addition and thus good approximations to band edges and fundamental
11 gaps from a density functional approximation (DFA) with minimal delocalization er-
12 ror. For other quasiparticle energies, their connection to the generalized Kohn-Sham
13 orbital energies has not been established but remains highly interesting. We provide the
14 comparison of experimental quasiparticle energies for many finite systems with calcula-
15 tions from the GW Green's function and localized orbitals scaling correction (LOSC),
16 a recently developed correction to semilocal DFAs, which has minimal delocalization
17 error. Extensive results with over forty systems clearly show that LOSC orbital ener-
18 gies achieve slightly better accuracy than the GW calculations with little dependence
19 on the semilocal DFA, supporting the use of LOSC DFA orbital energies to predict
20 quasiparticle energies. This also leads to the calculations of excitation energies of the
21 N -electron systems from the ground state DFA calculations of the $(N - 1)$ -electron
22 systems. Results show good performance with accuracy similar to TDDFT and the
23 delta SCF approach for valence excitations with commonly used DFAs with or without
24 LOSC. For Rydberg states, good accuracy was obtained only with the use of LOSC
25 DFA. This work highlights the pathway to quasiparticle and excitation energies from
26 ground density functional calculations.
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47 **Introduction**

48 Quasiparticles are a powerful concept in electronic structure theory of many-electron sys-
49 tems. In particular, accurate prediction of quasiparticle energies is essential for interpreting
50 the electronic excitation spectra of molecules and materials, such as photoemission and op-
51 tical experiments. Formally, quasiparticle energies can be exactly formulated in many-body
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3 perturbation theory.¹⁻³ In practice, the GW approximation⁴⁻⁷ is most widely used for bulk
4 simulations. Unfortunately, GW calculations are still expensive computationally. Therefore,
5 a low-cost alternative to GW approximation that offers good accuracy for the prediction of
6 quasiparticle energies is critical to the calculations of large-scale systems, and for efficient
7 high throughput study of materials.
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13 Kohn-Sham (KS) density functional theory (DFT),⁸⁻¹⁰ due to its good balance between
14 accuracy and computational tractability, is among the most popular and versatile methods
15 available for many-electron problems. In addition to the total electron energy, the physical
16 interpretation of the KS eigenvalues has also attracted great interest. It has been known
17 for decades that among the KS eigenvalues obtained from the exact functional, the highest
18 occupied molecular orbital (HOMO) energy, $\varepsilon_{\text{HOMO}}$, is negative vertical ionization poten-
19 tial (VIP), $-I$.¹⁰⁻¹⁷ In 2008, it was rigorously proven^{18,19} that within the generalized KS
20 (GKS) theory, which includes KS theory as a special case, the HOMO/LUMO energy is the
21 chemical potential, $(\frac{\partial E}{\partial N})_v$, for electron removal/addition from the DFAs for any DFA that
22 is a differentiable functional of the non-interacting one-electron density matrix in case of
23 GKS or the density in case of KS, and consequently approximation to $-I/A$ following
24 the Perdew-Parr-Levy-Baldur (PPLB) condition.^{11,20-22} Accurate approximation of $-I/A$
25 can thus be expected from the HOMO/LUMO energy of DFAs with minimum delocalization
26 error.²³ Therefore, the fundamental gap defined as $I - A$ can be exactly obtained from the
27 chemical potential difference, that is, the GKS HOMO-LUMO gap.
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43 In addition to HOMO and LUMO, the physical meaning of other GKS eigenvalues also
44 has great theoretical significance and application value. Of particular interest is the con-
45 nection between the GKS spectrum and the quasiparticle spectrum. Unfortunately, no clear
46 connection has been established, although there have been many attempts to approximately
47 attach some meanings to the occupied orbital energies within the KS theory. It has been
48 argued that the orbital energies below $\varepsilon_{\text{HOMO}}$ can be interpreted as other approximate prin-
49 ciple (sometimes called relaxed) VIPs, i.e., the ionized system being in an excited state.^{24,25}
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3 Recently, it has been argued that the correct occupied KS orbital energies should correspond
4 to the exact principle VIPs using the linear response time-dependent density functional the-
5 ory (LR-TDDFT) under the adiabatic approximation.²⁶⁻²⁸ However, it has been shown that
6 the adiabatic approximation within TDDFT is not generally valid.²⁹
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11 Even though no theorem has been rigorously established to link the remaining GKS
12 orbital energies to quasiparticle energies, it is still beneficial for practical applications to
13 construct a good density functional approximation (DFA) that can accurately predict quasi-
14 particle energies from orbital energies. For commonly used DFAs, such as local density
15 approximations (LDAs), generalized gradient approximations (GGAs) and hybrid GGAs,
16 their HOMO and LUMO energies are the corresponding chemical potentials but have large
17 systematic error in predicting $-I/ - A$.^{18,23} In particular, the HOMO energy is significantly
18 overestimated, which leads to underestimation of I ; while the LUMO energy is severely
19 underestimated, so that A is overestimated. Hence, the fundamental gap is significantly
20 underestimated by HOMO-LUMO gap of common DFAs. From the fractional charge per-
21 spective, this failure has been attributed^{18,23} to the violation of the PPLB condition^{11,20-22}
22 which requires the total energy, as a function of electron number, to be piecewise straight
23 lines interpolating between adjacent integer points. And the convex deviation suffered by
24 commonly used DFAs was identified as the delocalization error inherent in approximate
25 functionals.^{23,30,31} Other occupied and unoccupied orbitals follow the same trend as HOMO
26 and LUMO, respectively. Typically, energies of occupied orbitals (including HOMO) have
27 been seriously overestimated when serving as approximations to electron removal energies,
28 so that they cannot qualitatively reproduce experimental photoemission spectrum. It is thus
29 reasonable to believe that other orbitals should suffer similarly from the delocalization error
30 of approximate functionals.
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51 Following the perspective of fractional charges, there have been many attempts focusing
52 on removing delocalization error in approximate functionals. MCY3³² was the first DFA
53 constructed to restore the PPLB condition; long-range corrected (LC) functionals³³⁻³⁶ and
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doubly hybrid functionals^{37–39} show some promise on reproducing linear fractional charge behavior; tuned range-separated hybrid functionals^{40–42} impose extra constraints on orbital energies from total energy difference by optimizing the range-separation parameter for each system. All these functionals show significantly improvement on the calculations of HOMO and LUMO energies for small molecules. Extension to large and bulk systems lead to various issues. To achieve systematic elimination of the delocalization error associated with commonly used DFAs, recently developed localized orbital scaling correction (LOSC) functional⁴³ introduces a set of auxiliary localized orbitals (LOs), or orbitalets, and imposes PPLB condition on each of the LOs. As a result, LOSC can achieve size-consistent corrections to both the total energy and orbital energies.

Methods

To demonstrate that orbital energies $\varepsilon(N)$ of LOSC can give accurate approximation to quasiparticle/quasihole energies $\omega^{+/-}(N)$ for an N -electron system, for the description of electron addition/removal, i.e.

$$\begin{aligned}\varepsilon_m(N) &\approx \omega_m^+(N) = E_m(N+1) - E_0(N), \\ \varepsilon_n(N) &\approx \omega_n^-(N) = E_0(N) - E_n(N-1),\end{aligned}\tag{1}$$

we have already applied LOSC to generate accurate LUMO and HOMO energies for a broad range of atoms and molecules.⁴³ In Eq. 1, $\varepsilon_m(N)/\varepsilon_n(N)$ is a virtual/occupied GKS orbital energy for the N -electron system. The performance of LOSC for HOMO/LUMO and other GKS orbital energies will be examined extensively in present work.

Furthermore, Eq. 1 allows the calculation of excitation energies $\Delta E_m(N)$ at the cost of a ground-state DFT calculation via the particle part, relating to electron affinities (EAs), of

the quasiparticle spectrum of the $(N - 1)$ system, i.e.

$$\begin{aligned}
 \Delta E_m(N) &= E_m(N) - E_0(N) \\
 &= [E_m(N) - E_0(N - 1)] - [E_0(N) - E_0(N - 1)] \\
 &= \omega_m^+(N - 1) - \omega_{min}^+(N - 1) \\
 &\approx \varepsilon_m(N - 1) - \varepsilon_{LUMO}(N - 1),
 \end{aligned} \tag{2}$$

where $E_m(N)$ corresponds to the m th excitation of the N -electron system, and $E_0(N - 1)$ is the ground-state energy of $(N - 1)$ -electron system. $E_0(N) - E_0(N - 1)$ is $-A$ of the $(N - 1)$ system and can be obtained from $\omega_{min}^+(N - 1)$, the minimum of particle part of the quasiparticle spectrum, and approximated as $\varepsilon_{LUMO}(N - 1)$, the LUMO energy of the DFA calculation for the $(N - 1)$ system. The excitation energy $\Delta E_m(N)$ can thus be obtained as the virtual orbital energy difference $\varepsilon_m(N - 1) - \varepsilon_{LUMO}(N - 1)$ from a ground-state self-consistent field (SCF) calculation on $(N - 1)$ -electron system. In addition, Eq. 2 describes the excitations from HOMO to unoccupied orbitals (LUMO and above LUMO), due to the fact that N -electron system is retrieved by adding one electron to the virtual orbitals of a ground state $(N - 1)$ -electron system. Besides calculation from $(N - 1)$ -electron system, excitation energies can also be calculated similarly via the hole part, relating to ionization potentials (IPs), of the quasiparticle spectrum of the $(N + 1)$ system, i.e.

$$\begin{aligned}
 \Delta E_n(N) &= E_n(N) - E_0(N) \\
 &= [E_0(N + 1) - E_0(N)] - [E_0(N + 1) - E_n(N)] \\
 &= \omega_{max}^-(N + 1) - \omega_n^-(N + 1) \\
 &\approx \varepsilon_{HOMO}(N + 1) - \varepsilon_n(N + 1),
 \end{aligned} \tag{3}$$

where $E_0(N + 1) - E_0(N)$ is $-I$ of the $(N + 1)$ system and can be obtained from $\omega_{max}^-(N + 1)$, the maximum of the hole part in the quasiparticle spectrum, and approximated as

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3 $\varepsilon_{HOMO}(N + 1)$, the HOMO energy of the DFA calculation for the $(N + 1)$ system. The
4 excitation energies can thus be obtained as occupied orbital energy differences $\varepsilon_{HOMO}(N +$
5 $1) - \varepsilon_n(N + 1)$ from a ground-state SCF calculation on $(N + 1)$ -electron system. Being
6 different from the approach of $(N - 1)$ -electron calculation, Eq. 3 describes the excita-
7 tions from occupied orbitals (HOMO and HOMO below) to LUMO, since the N -electron
8 system is retrieved by removing one electron from the occupied orbitals of a ground state
9 $(N + 1)$ -electron system.
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Many theoretical approaches have been developed to calculate excitation energies. High-
level methods, including equation-of-motion coupled cluster (EOM-CC),⁴⁴⁻⁴⁶ linear-response
coupled cluster (LR-CC),⁴⁷⁻⁵⁰ multireference configuration interaction (MRCI),^{51,52} complete
active space configuration interaction (CASCI),⁵³⁻⁵⁵ CASPT2^{56,57} and others, can produce
accurate results, but significantly limited in system size and complexity. Other computation-
ally efficient methods, such as configuration interaction singles (CIS),^{58,59} time dependent
DFT (TDDFT)⁶⁰ and Δ SCF⁶¹ have been well-known to describe excitation energies with
success, meanwhile they have important weakness. Particularly, CIS can overestimate ex-
citation energy by 2 eV.⁵⁹ TDDFT^{59,62} and Δ SCF method⁶³⁻⁷⁰ typically yield results with
good accuracy, but TDDFT faces challenges to describe double,^{63,71,72} Rydberg⁷³⁻⁷⁶ and
charge transfer excitations⁷⁷⁻⁷⁹ with conventional DFAs. In contrast, Eqs. 2 and 3 provide
the simplest way to calculate excitation energies, with which various excitation energies can
be obtained after the corresponding ground-state SCF calculation. Obviously, the accuracy
of excitation energies from Eqs. 2 and 3 depends on the quality of DFA orbital energies, as
approximation to the quasiparticle energies.

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Next, we will show the test results of approximating quasiparticle energies (Eq. 1) and
excitation energies (Eqs. 2/3) by different DFAs and LOSC-DFAs. For the test of quasi-
particle energies, we compare IPs (the hole part of the quasiparticle spectrum) with occupied
orbital energies, as well as EA with LUMO energy. Other EAs from the particle part of the
quasiparticle spectrum are not tested in present work, as experimental data or accurate

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3 computational data is not available for comparison, and the calculation of these EAs is very
4 demanding on the basic functions (much harder to calculate than the EA from LUMO en-
5 ergy). For the test of quasiparticle energies, 40 molecules with conjugated system (up to
6 large system like C₆₀) were selected from Blase's⁸⁰ and Marom's⁸¹ test set to calculate pho-
7 toemission spectrum, HOMO and LUMO energies. Polyacenes (n=1-6), water, ethylene and
8 thiophene are used to study the valence orbital energies as approximation to the correspond-
9 ing quasiparticle energies. For the test of excitation energies, 16 molecules are obtained from
10 Ref 82 as a molecular set to test the low-lying excitation energies. Four atoms (Li, Be, Mg,
11 and Na) are selected as an atomic set to test their excitation energies up to Rydberg states.
12 The QM4D package⁸³ was used to perform the DFT calculations. Several conventional func-
13 tionals, such as local density approximation (LDA),^{84,85} PBE,⁸⁶ BLYP^{87,88} and B3LYP,⁸⁷⁻⁸⁹
14 and LOSC-DFAs were tested. For LOSC calculations, the post-SCF procedure was applied.
15 More details of computations and test results can be found in SI.
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31 Results & Discussion

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34 First, HOMO and LUMO energies of different DFAs and LOSC-DFAs are compared. Table 1
35 summarizes mean absolute errors (MAEs) of orbital energies in comparison with experimen-
36 tal quasiparticle energies, where self-consistent GW (scGW)^{5,7} and G0W0^{4,5} results are also
37 included for comparison. Previously, it has been shown that LOSC can size-consistently
38 improve HOMO and LUMO energies on systems range from small sized molecules to poly-
39 mers.⁴³ Here, we further calculated a set of 40 organic molecules, where the molecular size
40 is much larger than that of the G2-97 set tested before. Due to the serious delocalization
41 error,^{18,23} LDA and PBE show systematic underestimation of VIPs and overestimation of
42 VEAs, with MAEs larger than 2.0 eV; hybrid functional B3LYP performs slightly better
43 with a 20% reduction in error, but the results still qualitatively deviate from the exper-
44 iment. LOSC-DFAs significantly improve both HOMO and LUMO energies, with MAEs
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Table 1: Mean absolute errors (MAEs, in eV) of orbital energies compared with experimental quasi-particle energies. Experimental reference were obtained from Ref. 80,81.

	HOMO ^a	LUMO ^a	Valence ^b
scGW ^c	0.47	0.34	-
G ₀ W ₀ @PBE ^c	0.51	0.37	-
LOSC-LDA	0.34	0.48	0.69 (0.53)
LOSC-PBE	0.37	0.33	0.60 (0.35)
LOSC-B3LYP	0.26	0.29	0.43 (0.36)
LDA	2.58	2.43	3.06 (2.33)
PBE	2.81	2.16	3.23 (2.55)
B3LYP	2.00	1.57	2.24 (1.79)
Δ-DFA ^d	0.43	0.26	0.70 (0.73)
Δ-LOSC-DFA ^d	0.34	0.38	0.41 (0.26)

^a 40 molecules are chosen from Refs. 80 and 81 for the calculation of HOMO and LUMO energies. The size of these molecules ranges from small aromatic ring, like thiophene, to large conjugated system, like C₆₀. These molecules are thiophene, benzothiadiazole, benzothiazole, fluorene, H₂P, H₂PC, H₂TPP, PTCDA, thiadiazole, benzoquinone, Cl₄-isobenzofuranedione, dichlone, F₄-benzoquinone, maleicanhydride, nitrobenzene, phenazine, phthalimide, TCNE, benzonitrile, Cl₄-benzoquinone, dinitrobenzonitrile, F4-benzenedicarbonitrile, fumaronitrile, mDCNB, NDCA, nitrobenzonitrile, phthalic anhydride, TCNQ, acridine, azulene, bodipy, naphthalenedione, C₆₀, C₇₀, and polyacenes (n = 1 - 6).

^b Overall, 51 valence orbital energies, from HOMO to orbitals below HOMO in order, are calculated for polyacenes (n = 1 - 6), water, ethylene and thiophene, and compared with the available experimental IPs. Numbers shown in the parenthesis are the MAE of polyacenes, which is listed as well to verify the size-consistency.

^c GW results were taken from Ref 81.

^d PBE functional was used in HOMO and LUMO calculation. BLYP functional was used in valence orbital results.

much smaller than their parent DFAs. In particular, MAEs of LOSC-B3LYP are smaller than 0.3 eV. It is also interesting to compare LOSC with the well-recognized scGW and G₀W₀ methods. We find that LOSC can achieve better accuracy than scGW and G₀W₀ methods for HOMO and LUMO energy calculations. Our results also show that starting from the same reference DFA (PBE), LOSC (MAE of HOMO 0.37 eV and of LUMO 0.33 eV) outperforms the G₀W₀ (MAE of HOMO 0.51 eV and of LUMO 0.37 eV). It is well-known that the G₀W₀ calculation is significantly influenced by the reference DFAs. In contrast, LOSC

can provide similar accuracy based on different parent DFAs, including hybrid functionals.

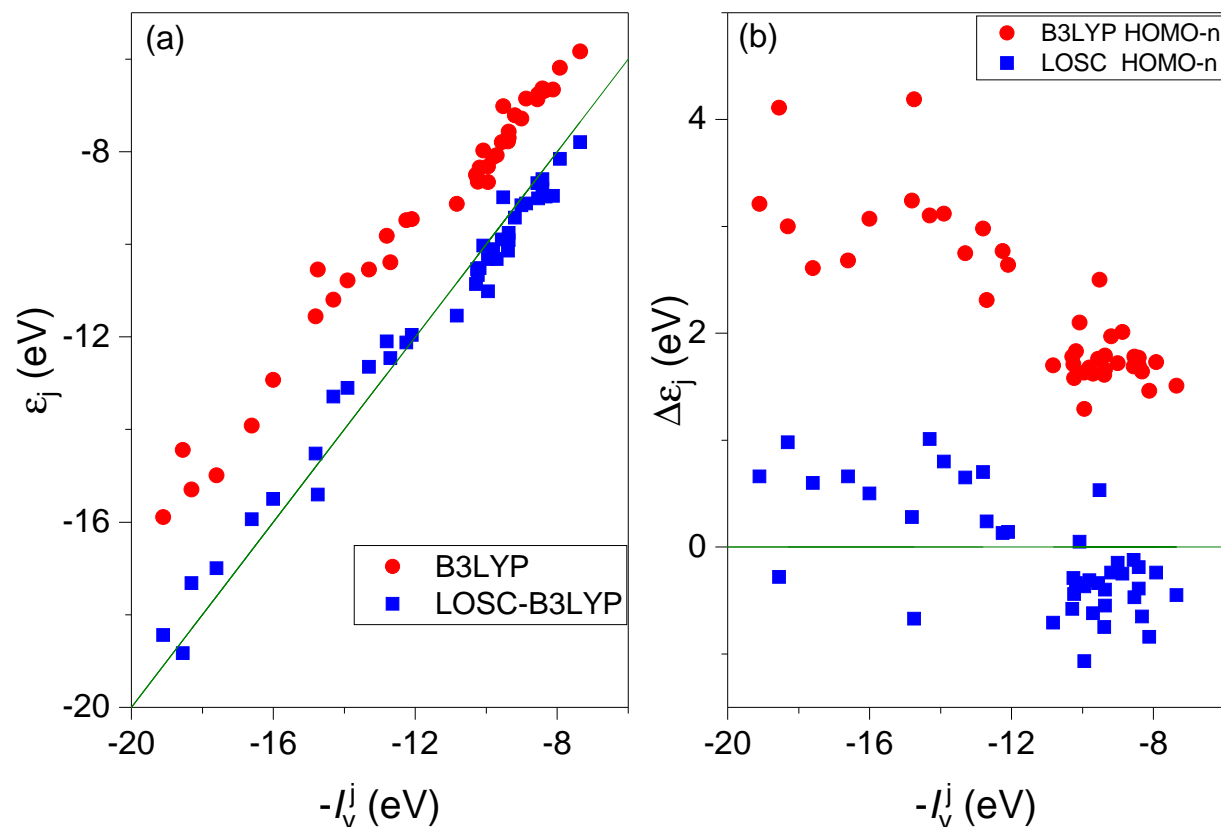


Figure 1: Calculated ϵ_j of B3LYP and LOSC-B3LYP in comparison with the experimental $-I_v^j$. (a) Orbital energies ϵ_j for 43 states below HOMO are included. The solid line indicates $\epsilon_j = -I_v^j$. (b) The errors of calculated orbital energies with respect to the experimental negative VIPs, $\Delta\epsilon_j = \epsilon_j + I_v^j$, are recorded.

Besides HOMO and LUMO, Table 1 also summarizes the valence orbital energies from DFAs and LOSC-DFAs. Similarly, we notice that the orbital energies from commonly used DFAs show serious deviation from the experimental reference (above 2 eV MAE), while LOSC-DFAs can largely reduce the error (0.43 - 0.69 eV). Moreover, we also observe from Table 1 that LOSC gives slightly larger absolute error when comparing valence orbital energies with HOMO/LUMO energies. Since valence orbitals are much larger (up to 20 eV) than HOMO and LUMO (mostly below 10 eV) energies, making larger correction from LOSC desired, it is more difficult to achieve the same level of accuracy for valence orbital energies. This fact suggests that further development of LOSC is still needed for better valence orbital

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3 energies. Besides Table 1, the largely reduced error for valence orbital energies by LOSC
4 can be clearly seen from Figure 1(a) and Figure 1(b): valence orbital energies of B3LYP
5 significantly overestimate quasiparticle energies; with LOSC, the systematic error is elimi-
6 nated. By further observing Figure 1(b), we find that the overestimation of quasiparticle
7 energies by B3LYP becomes more serious for states with lower energies, which is corrected in
8 LOSC-B3LYP. In addition, the results of polyacenes (n=1-6), of which the chain length keeps
9 increasing, are shown in Table 1 to study the performance of size-consistency. It clear shows
10 that MAEs of valence orbital energies from LOSC-DFAs maintain at low level, meanwhile
11 the MAE of results from Δ -LOSC-BLYP (0.26 eV) is much better than Δ -BLYP (0.73 eV).
12 Therefore, it supports that LOSC can size-consistently correct the valence orbital energies,
13 as well as the total energy of high level states calculated in Δ SCF approach.
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25 To further confirm that LOSC is a reliable method for the calculation of quasiparticle
26 energies, GKS spectra of forty systems were plotted and compared to the experimental
27 photoemission spectra, along with GW results when available. Figure 2 only show the results
28 of azulene and benzonitrile; tests on other molecules give similar results, which can be found
29 in SI. As can be seen, commonly used DFAs exemplified by PBE and B3LYP give too narrow
30 HOMO-LUMO gaps, with the occupied levels being significantly overestimated and LUMO
31 energy being underestimated. LOSC greatly corrects the results. Furthermore, spectra by
32 LOSC-DFAs are consistent with the experimental photoemission spectra, with the principle
33 peaks appearing at the same positions. Overall, LOSC shows little dependence on parent
34 DFAs, and can reach an accuracy that is comparable to that of GW methods in predicting
35 quasiparticle spectra. Note that, although there existed some approaches in GW methods
36 to reduce the computational scaling, such as stochastic GW,^{92,93} the GW calculation is still
37 computationally expensive in general. From LOSC-DFAs calculation, the computational
38 cost of LOSC only amounts to a small portion of the parent functional, thus maintaining it
39 at the DFT calculation level. Therefore, LOSC-DFAs are a promising low-cost alternative
40 to GW approximation for accurate prediction of quasiparticle energies.
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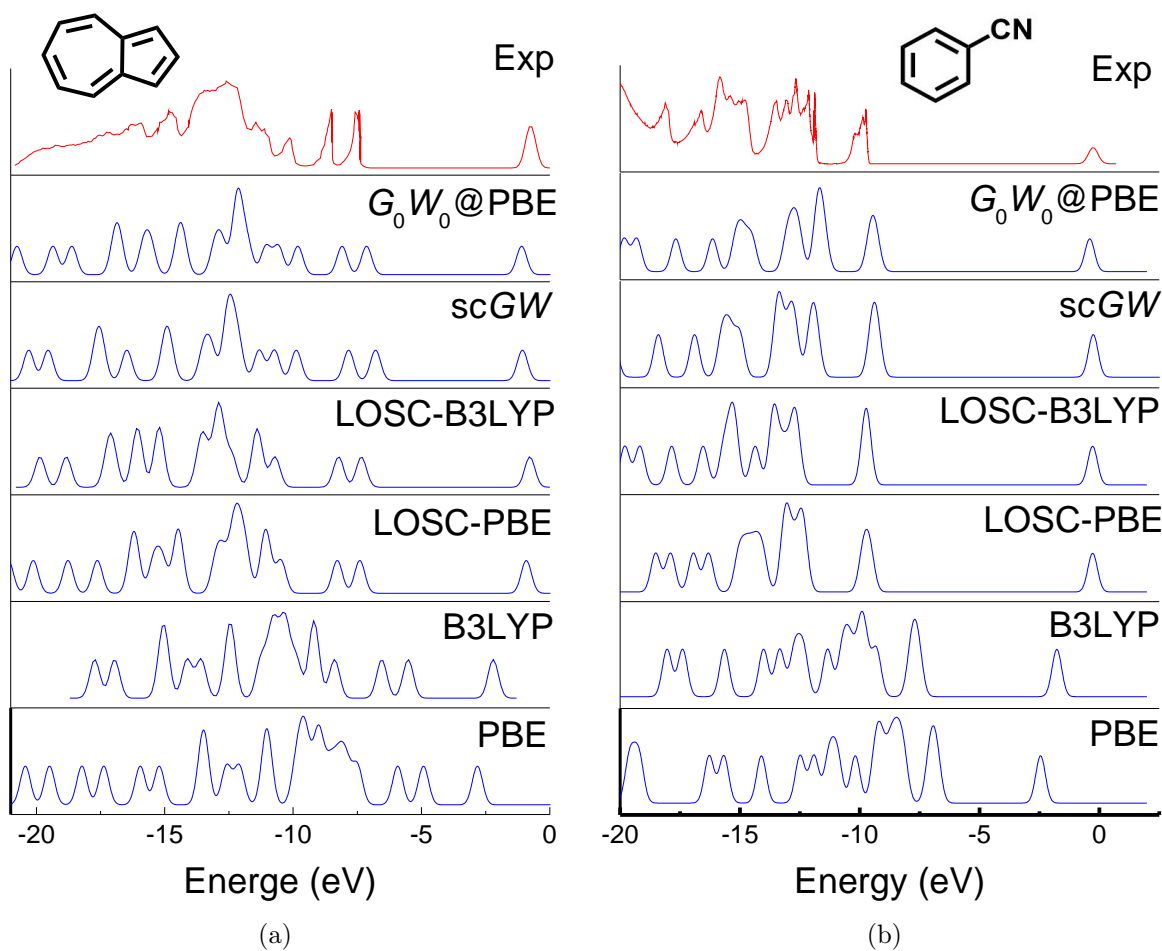


Figure 2: Photoemission spectrum of (a) azulene and (b) benzonitrile. Experimental results are obtained from (a) Ref 90 and (b) Ref 91. The rightmost peak in the experimental spectrum corresponds to the electron affinity (EA), and it is broadened by a Gaussian function with a width of 0.2 eV around experimental EA value. The calculated spectrum from DFT are broadened from orbital energies (occupied orbitals and LUMO) by the same type of Gaussian functions. scGW and G_0W_0 results are obtained from Ref 81.

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Accurate prediction of quasiparticle energies by LOSC-DFAs thus allows the calculation of excitation energies from ground state DFT calculation through Eqs. 2 and 3. However, calculation of anionic molecule ($N + 1$ -electron system) normally requires good choice of diffused basis set,⁹⁴ making results from ($N + 1$)-electron system calculation dependent on the quality of applied basis set. A reasonable basis set for ($N - 1$)-electron system calculations like cc-pVTZ can be too small for ($N + 1$)-electron system calculations, yielding an unbound electron. Due to this effect, the orbital energies, especially HOMO, of ($N + 1$)-electron system are not reliable and lead to poor HOMO-LUMO excitation energies compared with ($N - 1$)-electron system calculation. Although one can use a large basis set to perform reasonable ($N + 1$)-electron system calculations, this is not computationally economical. Considering these aspects, we mainly focus on discussing the excitation energies calculated from ($N - 1$)-electron systems in the main text; some results from ($N + 1$)-electron systems can be found in SI. For the excitations of HOMO to orbitals above HOMO, starting from the doublet ground state of ($N - 1$)-electron systems (assuming one more α -spin electron than β -spin electrons), there are two orbital energies of different spins for each orbital above HOMO. Apparently, α -spin orbital energies should be used for triplet excitations. For singlet excitations, a spin purification process similar to Refs. 61 and 69 is used here, and the excitation energies are calculated by

$$\Delta E_m^{\text{singlet}}(N) \approx [2\varepsilon_m^\beta(N - 1) - \varepsilon_m^\alpha(N - 1)] - \varepsilon_{\text{HOMO}}^\beta(N - 1). \quad (4)$$

The results of 48 low-lying excitation energies obtained from different DFAs and LOSC-DFAs are summarized in Table 2, where triplet and singlet excitations are categorized and presented. The results from Hartree Fock (HF), TDDFT and Δ SCF-DFT with B3LYP functional are also listed for comparison. As expected, LOSC-DFAs can provides good prediction for excitation energies due to their excellent performance on quasiparticle energies. Especially, the total MAE and MSE of LOSC-B3LYP are 0.49 eV and -0.19 eV, which are

Table 2: Mean absolute errors (MAEs, in eV) and mean sign errors (MSEs, in eV) of 48 low-lying excitation energies obtained from HF, DFT, TDDFT and Δ SCF-B3LYP calculation on 16 molecules. Notation T1 refers to triplet HOMO to LUMO excitation, and T2 refers to triplet HOMO to LUMO+1 excitation. The analogy notation for S1 and S2 which stand for singlet excitations. Reference data were obtained from Ref 95.

Method	T1		T2		S1		S2		Total	
	MAE	MSE	MAE	MSE	MAE	MSE	MAE	MSE	MAE	MSE
HF	1.08	-0.88	2.04	-1.23	1.12	-0.59	1.49	0.81	1.35	-0.83
BLYP	0.19	-0.14	0.63	-0.10	0.68	-0.65	0.65	-0.24	0.53	-0.22
B3LYP	0.17	-0.13	0.43	0.01	0.45	-0.33	0.67	-0.58	0.42	-0.01
LDA	0.24	-0.02	0.65	0.04	0.73	-0.68	0.70	-0.27	0.58	-0.16
LOSC-BLYP	0.49	-0.28	0.46	-0.37	0.84	-0.84	0.62	0.10	0.63	-0.44
LOSC-B3LYP	0.30	-0.23	0.28	-0.14	0.60	-0.51	0.69	-0.29	0.49	-0.19
LOSC-LDA	0.48	-0.18	0.52	-0.27	0.88	-0.88	0.71	0.11	0.67	-0.42
TD-B3LYP	0.45	-0.45	0.39	-0.39	0.38	-0.35	0.28	0.27	0.38	-0.37
Δ -SCF	0.20	-0.16	0.33	-0.24	0.56	-0.56	0.18	0.04	0.35	-0.31

comparable to TDDFT (MAE of 0.38 eV and MSE of -0.37 eV) and Δ SCF-DFT (MAE of 0.35 eV and MSE of -0.31 eV, based on the same reference DFA (B3LYP)). For conventional DFAs, it is surprising to find that they have very good performance on predicting low-lying excitation energies, even though they perform poorly in quasiparticle energy calculations. These good results should be attributed to the fact that unoccupied (or occupied) orbitals that are energetically close suffer from a similar amount of systematic delocalization error, making the error cancellation when calculating excitation energies from the difference of orbital energies. This can be seen clearly by comparing their performance on the T1 (HOMO-LUMO excitation) and T2 (HOMO-(LUMO+1) excitation). Conventional DFAs tested here perform very well on T1 excitation (MAEs are around 0.2 eV), but their performance on T2 excitation is much worse (MAEs can be larger than 0.6 eV). In contrast, LOSC-DFAs are consistent in their performance for these two types of excitations. Thus, it can be inferred that for a DFT method to achieve good accuracy for the prediction of excitation energies of low- to high-lying states, it is necessary to provide consistently reliable quasiparticle energies for all different states involved.

Table 3: Mean absolute errors (MAEs, in eV) and mean sign errors (MSEs, in eV) with respect to experimental reference of excitation energies of 4 atoms from low-lying states to Rydberg states. 12 excitations were included for each atom. Experimental values were obtained from Ref 96.

		LDA	BLYP	B3LYP	LOSC-LDA	LOSC-BLYP	LOSC-B3LYP
Be singlet ^a	MAE	2.37	1.15	1.85	0.24	0.54	0.35
	MSE	2.37	-1.15	1.85	0.07	-0.29	-0.06
Be triplet ^a	MAE	2.30	1.91	1.79	0.28	0.60	0.30
	MSE	2.11	1.68	1.79	-0.04	-0.60	-0.29
Mg singlet ^b	MAE	2.37	2.07	1.69	0.55	0.26	0.21
	MSE	2.37	2.07	1.69	0.55	0.16	0.21
Mg triplet ^b	MAE	2.13	1.82	1.54	0.40	0.15	0.14
	MSE	2.12	1.80	1.52	0.34	-0.11	0.06
Li doublet ^a	MAE	0.97	1.77	1.40	0.91	0.17	0.16
	MSE	0.97	1.77	1.40	-0.89	0.04	-0.03
Na doublet ^b	MAE	1.52	2.16	1.69	0.25	0.57	0.42
	MSE	1.52	2.16	1.69	-0.11	0.57	0.42

^a The excitation states are calculated up to atomic orbital 6p.

^b The excitation states are calculated up to atomic orbital 7p.

To further confirm the above inference, we chose four atoms (Li, Be, Mg, and Na) to test their excitation energies up to Rydberg states. Such choice of atomic set is due to the availability of their experimental references and clear picture of Rydberg states from atoms, in which one electron is excited to a high-level atomic orbital. Table 3 summarizes the MAEs from different DFAs and LOSC-DFAs applied to this atomic test set, more detailed results can be found in SI. As can be seen, conventional DFAs show large MAEs for all the four atoms. By observing Tabs. S7 to S12 for these test atoms in SI, it is easy to find that the higher the excited states, the greater the deviation between the results obtained by DFAs and the experimental values. This is because conventional DFAs show larger errors for quasiparticle energies at higher states, thus the difference of orbital energies cannot completely offset the systematic delocalization errors of orbitals that are energetically far apart. In contrast, LOSC-DFAs perform similarly for different excited states with very high accuracy, which should be attributed to the good performance of LOSC on quasiparticle energies of different states.

Conclusions

In conclusion, we have carried out a comprehensive test on calculations of quasiparticle energies and excitation energies with the LOSC functional and DFAs. Through a large number of comparisons with experimental results and GW results, we demonstrated that LOSC-DFAs shows little dependence on parent DFAs, and can reach an accuracy that is better or comparable to that of GW methods in predicting quasiparticle spectra. This also leads to the calculations of excitation energies of the N -electron systems from ground state calculations of the $(N - 1)$ -electron systems. Commonly used DFAs show good performance for valence excitations, but not accurate for higher energy and Rydberg states; in contrast, LOSC-DFAs can provide consistently accurate results for excitation energies from low-lying to Rydberg states for the tested cases. This work highlights the pathway to quasiparticle and excitation energies from ground density functional calculations.

Note. When preparing the manuscript for submission, we became aware of Ref. 97, which also calculated excitation energies from orbital energy differences of the $(N - 1)$ -electron systems. Different functionals from our tests and only valence excitations were reported.

Supporting Information Available

- SI.pdf: More details of computations and test results.

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Graphical TOC Entry

