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

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Abstract

Quasiparticle energies and fundamental band gaps in particular are critical properties of molecules and materials. It was rigorously established that the generalized Kohn-Sham HOMO and LUMO orbital energies are the chemical potentials of electron removal and addition and thus good approximations to band edges and fundamental gaps from a density functional approximation (DFA) with minimal delocalization error. For other quasiparticle energies, their connection to the generalized Kohn-Sham orbital energies has not been established but remains highly interesting. We provide the comparison of experimental quasiparticle energies for many finite systems with calculations from the GW Green's function and localized orbitals scaling correction (LOSC), a recently developed correction to semilocal DFAs, which has minimal delocalization error. Extensive results with over forty systems clearly show that LOSC orbital energies achieve slightly better accuracy than the GW calculations with little dependence on the semilocal DFA, supporting the use of LOSC DFA orbital energies to predict quasiparticle energies. This also leads to the calculations of excitation energies of the $N$-electron systems from the ground state DFA calculations of the $(N - 1)$-electron systems. Results show good performance with accuracy similar to TDDFT and the delta SCF approach for valence excitations with commonly used DFAs with or without LOSC. For Rydberg states, good accuracy was obtained only with the use of LOSC DFA. This work highlights the pathway to quasiparticle and excitation energies from ground density functional calculations.
Graphical TOC Entry

![Graphical representation of experimental and computational results for energy levels.

- Experiment (Exp)
- LOSC-PBE
- scGW
- G\textsubscript{W}\textsubscript{0}@PBE
- PBE

Energy (eV) vs Various Computational Methods and Experimental Results.
Quasiparticles are a powerful concept in electronic structure theory of many-electron systems. In particular, accurate prediction of quasiparticle energies is essential for interpreting the electronic excitation spectra of molecules and materials, such as photoemission and optical experiments. Formally, quasiparticle energies can be exactly formulated in many-body perturbation theory. In practice, the GW approximation is most widely used for bulk simulations. Unfortunately, GW calculations are still expensive computationally. Therefore, a low-cost alternative to GW approximation that offers good accuracy for the prediction of quasiparticle energies is critical to the calculations of large-scale systems, and for efficient high-throughput study of materials.

Kohn-Sham (KS) density functional theory (DFT), due to its good balance between accuracy and computational tractability, is among the most popular and versatile methods available for many-electron problems. In addition to the total electron energy, the physical interpretation of the KS eigenvalues has also attracted great interest. It has been known for decades that among the KS eigenvalues obtained from the exact functional, the highest occupied molecular orbital (HOMO) energy, $\varepsilon_{\text{HOMO}}$, is negative vertical ionization potential (VIP), $-I$. In 2008, it was rigorously proven that within the generalized KS (GKS) theory, which includes KS theory as a special case, the HOMO/LUMO energy is the chemical potential, $(\frac{\partial E}{\partial N})_v$, for electron removal/addition from the DFAs for any DFA that is a differentiable functional of the non-interacting one-electron density matrix in case of GKS or the density in case of KS, and consequently approximation to $-I - A$ following the Perdew-Parr-Levy-Balduz (PPLB) condition. Accurate approximation of $-I - A$ can thus be expected from the HOMO/LUMO energy of DFAs with minimum delocalization error. Therefore, the fundamental gap defined as $I - A$ can be exactly obtained from the chemical potential difference, that is, the GKS HOMO-LUMO gap.

In addition to HOMO and LUMO, the physical meaning of other GKS eigenvalues also has great theoretical significance and application value. Of particular interest is the connection between the GKS spectrum and the quasiparticle spectrum. Unfortunately, no clear
connection has been established, although there have been many attempts to approximately attach some meanings to the occupied orbital energies within the KS theory. It has been argued that the orbital energies below $\varepsilon_{\text{HOMO}}$ can be interpreted as other approximate principal (sometimes called relaxed) VIPs, i.e., the ionized system being in an excited state.$^{24,25}$ Recently, it has been argued that the correct occupied KS orbital energies should correspond to the exact principle VIPs using the linear response time-dependent density functional theory (LR-TDDFT) under the adiabatic approximation.$^{26-28}$ However, it has been shown that the adiabatic approximation within TDDFT is not generally valid.$^{29}$

Even though no theorem has been rigorously established to link the remaining GKS orbital energies to quasiparticle energies, it is still beneficial for practical applications to construct a good density functional approximation (DFA) that can accurately predict quasiparticle energies from orbital energies. For commonly used DFAs, such as local density approximations (LDAs), generalized gradient approximations (GGAs) and hybrid GGAs, their HOMO and LUMO energies are the corresponding chemical potentials but have large systematic error in predicting $-I/A$. In particular, the HOMO energy is significantly overestimated, which leads to underestimation of $I$; while the LUMO energy is severely underestimated, so that $A$ is overestimated. Hence, the fundamental gap is significantly underestimated by HOMO-LUMO gap of common DFAs. From the fractional charge perspective, this failure has been attributed to the violation of the PPLB condition which requires the total energy, as a function of electron number, to be piecewise straight lines interpolating between adjacent integer points. And the convex deviation suffered by commonly used DFAs was identified as the delocalization error inherent in approximate functionals.$^{23,30,31}$ Other occupied and unoccupied orbitals follow the same trend as HOMO and LUMO, respectively. Typically, energies of occupied orbitals (including HOMO) have been seriously overestimated when serving as approximations to electron removal energies, so that they cannot qualitatively reproduce experimental photoemission spectrum. It is thus reasonable to believe that other orbitals should suffer similarly from the delocalization error.
Following the perspective of fractional charges, there have been many attempts focusing on removing delocalization error in approximate functionals. MCY\textsuperscript{32} was the first DFA constructed to restore the PPLB condition; long-range corrected (LC) functionals\textsuperscript{33–36} and doubly hybrid functionals\textsuperscript{37–39} show some promise on reproducing linear fractional charge behavior; tuned range-separated hybrid functionals\textsuperscript{40,41} 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) functional\textsuperscript{42} 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.

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.

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

(1)

we have already applied LOSC to generate accurate LUMO and HOMO energies for a broad range of atoms and molecules.\textsuperscript{42} 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 of the quasiparticle spectrum of the 
\((N - 1)\) system, i.e.

\[
\Delta E_m(N) = E_m(N) - E_0(N) \\
= [E_m(N) - E_0(N - 1)] - [E_0(N) - E_0(N - 1)] \\
= \omega_m^+(N - 1) - \omega_{\text{min}}^+(N - 1) \\
\approx \varepsilon_m(N - 1) - \varepsilon_{\text{LUMO}}(N - 1),
\]

(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 \(\omega_{\text{min}}^+(N - 1)\), the minimum of particle part of the quasiparticle spectrum, and approximated as \(\varepsilon_{\text{LUMO}}(N - 1)\), 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 \(\varepsilon_m(N - 1) - \varepsilon_{\text{LUMO}}(N - 1)\) from a ground-state self-consistent field (SCF) calculation on \((N - 1)\)-electron system. Similarly, excitation energies can also be calculated via the hole part of the quasiparticle spectrum of the \((N + 1)\) system, i.e.

\[
\Delta E_n(N) = E_n(N) - E_0(N) \\
= [E_0(N + 1) - E_0(N)] - [E_0(N + 1) - E_n(N)] \\
= \omega_{\text{max}}^-(N + 1) - \omega_n^-(N + 1) \\
\approx \varepsilon_{\text{HOMO}}(N + 1) - \varepsilon_n(N + 1),
\]

(3)

where \(E_0(N + 1) - E_0(N)\) is -\(I\) of the \((N + 1)\) system and can be obtained from \(\omega_{\text{max}}^-(N + 1)\), the maximum of the hole part in the quasiparticle spectrum, and approximated as \(\varepsilon_{\text{HOMO}}(N + 1)\), the HOMO energy of the DFA calculation for the \((N + 1)\) system. The
Excitation energies can thus be obtained as occupied orbital energy differences $\varepsilon_{\text{HOMO}}(N+1) - \varepsilon_n(N+1)$ from a ground-state SCF calculation on $(N+1)$-electron system.

Many theoretical approaches have been developed to calculate excitation energies. High-level methods, including equation-of-motion coupled cluster (EOM-CC), linear-response coupled cluster (LR-CC), multireference configuration interaction (MRCI), complete active space configuration interaction (CASSCF), CASPT2 and others, can produce accurate results, but significantly limited in system size and complexity. Other computationally efficient methods, such as configuration interaction singles (CIS), time dependent DFT (TDDFT) and $\Delta$SCF have been well-known to describe excitation energies with success, meanwhile they have important weakness. Particularly, CIS can overestimate excitation energy by 2 eV. TDDFT and $\Delta$SCF method typically yield results with good accuracy, but TDDFT faces challenges to describe double, Rydberg and charge transfer excitations. 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.

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 quasiparticle energies, 40 molecules were selected from Blase’s and Marom’s test set to calculate photoemission spectrum, HOMO and LUMO energies. Polyacene (n=1-6) and other three small molecules are used to study the valence orbital energies as approximation to the corresponding quasiparticle energies. For the test of excitation energies, 16 molecules are obtained from Ref. as a molecular set to test the low-lying excitation energies. Four atoms (Li, Be, Mg, and Na) are selected as an atomic set to test their excitation energies up to Rydberg states. The QM4D package was used to perform the DFT calculations. Several conventional functionals, such as local density approximation (LDA), PBE, BLYP and
B3LYP,\textsuperscript{85–87} and LOSC-DFAs were tested. For LOSC calculations, the post-SCF procedure was applied. More details of computations and test results can be found in SI.

Table 1: Mean absolute errors (MAEs, in eV) of orbital energies compared with experimental quasi-particle energies. Experimental reference were obtained from Ref. 79,80.

|             | HOMO \textsuperscript{a} | LUMO \textsuperscript{a} | Valence \textsuperscript{b} |
|-------------|--------------------------|--------------------------|---------------------------|
| scGW \textsuperscript{c} | 0.47                     | 0.34                     | -                         |
| G\textsubscript{0}W\textsubscript{0}@PBE \textsuperscript{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)               |
| ∆-DFA \textsuperscript{d}   | 0.43                     | 0.26                     | 0.70 (0.73)               |
| ∆-LOSC-DFA \textsuperscript{d} | 0.34                     | 0.38                     | 0.41 (0.26)               |

\textsuperscript{a} MAE of HOMO and LUMO energies are based on the results of 40 test molecules.
\textsuperscript{b} MAE of valence orbital energies (HOMO and below HOMO) are based on 51 states of polyacene (n = 1 - 6) and other three small molecules. MAE of polyacene set were listed in the parenthesis.
\textsuperscript{c} GW results were taken from Ref 80.
\textsuperscript{d} PBE functional was used in HOMO and LUMO calculation. BLYP functional was used in valence orbital results.

First, HOMO and LUMO energies of different DFAs and LOSC-DFAs are compared. Tab. 1 summarizes mean absolute errors (MAEs) of orbital energies in comparison with experimental quasiparticle energies, where self-consistent GW (scGW)\textsuperscript{5,7} and G0W0\textsuperscript{4,5} results are also included for comparison. Previously, it has been shown that LOSC can size-consistently improve HOMO and LUMO energies on systems range from small sized molecules to polymers.\textsuperscript{42} Here, we further calculated a set of 40 organic molecules, where the molecular size is much larger than that of the G2-97 set tested before. Due to the serious delocalization error,\textsuperscript{18,23} LDA and PBE show systematic underestimation of VIPs and overestimation of VEA, with MAEs larger than 2.0 eV; hybrid functional B3LYP performs slightly better with a 20% reduction in error, but the results still qualitatively deviate from the experiment. LOSC-DFAs significantly improve both HOMO and LUMO energies, with
MAEs 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) out-performs 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.

![Diagram](image)

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

Besides HOMO and LUMO, Tab. 1 also summarizes the results of valence orbital energies from DFAs and LOSC-DFAs. Similarly, the serious deviation from the experiment by
commonly used DFAs can be largely reduced by LOSC. This can be clearly seen from Fig. 1: valence orbital energies of B3LYP significantly overestimate quasiparticle energies; with LOSC, the systematic error is eliminated. By observing Fig. 1(b), we find that the overestimation of quasiparticle energies by B3LYP becomes more serious for states with lower energies, which is corrected in LOSC-B3LYP.

![Diagram](image)

Figure 2: Photoemission spectrum of (a) azulene and (b) benzonitrile. All the calculated spectrum are broadened by Gaussian expansion with 0.2 eV. scGW and $G_0W_0$ results are obtained from Ref 80. Experimental results are obtained from (a) Ref 88 and (b) Ref 89.

To further confirm that LOSC is a reliable method for the calculation of quasiparticle energies, GKS spectra of forty systems were plotted and compared to the experimental photoemission spectra, along with GW results when available. Fig. 2 only shows the results of azulene and benzonitrile; tests on other molecules give similar results, which can be
found in SI. As can be seen, commonly used DFAs exemplified by PBE and B3LYP give
too narrow HOMO-LUMO gaps, with the occupied levels being significantly overestimated
and LUMO energy being underestimated. LOSC greatly corrects the results. Furthermore,
spectra by LOSC-DFAs are consistent with the experimental photoemission spectra, with
the principle peaks appearing at the same positions. Overall, LOSC shows little dependence
on parent DFAs, and can reach an accuracy that is comparable to that of GW methods in
predicting quasiparticle spectra. Note that the computational cost of LOSC only amounts to
a small portion of the parent functional, thus it is computationally much more efficient than
G0W0. Therefore, LOSC-DFAs are a promising low-cost alternative to GW approximation
for accurate prediction of quasiparticle energies.

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. Because
anionic systems ((N + 1)-electron systems) are generally difficult to converge to right states,
here we only discuss the excitation energies calculated from (N − 1)-electron systems; 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
Ref. 60 and ? is used here, and the excitation energies are calculated by

\[ \Delta E_{m}^{\text{singlet}} (N) \approx [2\varepsilon_{m} (N - 1) - \varepsilon_{m} (N - 1)] - \varepsilon_{\text{HOMO}} (N - 1). \]  (4)

The results of 48 low-lying excitation energies obtained from different DFAs and LOSC-
DFAs are summarized in Tab. 2, where triplet and singlet excitations are categorized and
presented. The results from Hartree Fock (HF), TDDFT and ∆SCF-DFT with B3LYP
functional are also listed for comparison. As expected, LOSC-DFAs can provides good
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 ∆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 90.

| 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    |
| ∆-SCF          | 0.20| -0.16    | 0.33| -0.24    | 0.56| -0.56    | 0.18| 0.04     | 0.35  | -0.31    |

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 comparable to TDDFT (MAE of 0.38 eV and MSE of -0.37 eV) and ∆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 91.

|                  | 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, four atoms (Li, Be, Mg, and Na) are selected as an atomic set to test their excitation energies up to Rydberg states. 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 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.
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. 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. 92, 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.

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**Supporting Information Available**

The following files are available free of charge.
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Description of LOSC calculation

If not specified, the LOSC calculation in this paper is carried out as a post self-consistent (post-SCF) correction to the parent functional results. In particularly, we first perform conventional DFT calculations with the parent functional to obtain the canonical orbitals \( \{ \varphi_i \} \) and the orbital energies \( \{ \epsilon_i \} \). Then with the restrained Boys localization (see Ref S1 for details), we obtain the localized orbitals \( \{ \phi_i \} \). Finally the energy correction and orbital energy corrections are given by

\[
\Delta E^{\text{LOSC}} = \sum_{ij} \frac{1}{2} \kappa_{ij} \lambda_{ij} (\delta_{ij} - \lambda_{ij}), \tag{1}
\]

and

\[
\Delta \epsilon_i = \sum_j \kappa_{jj} \left( \frac{1}{2} - \lambda_{jj} \right) |U_{ji}|^2 - \sum_{j \neq l} \kappa_{jl} \lambda_{jl} U_{ji} U_{li}^*. \tag{2}
\]
One can also perform self-consistent field (SCF) calculation for the LOSC, however, it has been demonstrated in Ref S1 that for small and compact molecules, the SCF only slightly differs from the post-SCF results, especially for the orbital energy calculations. So in this paper, we stick with the post-SCF calculations, which is computationally more efficient without much sacrifice in the accuracy of the results. The double integrals in the curvature formula have been evaluated using the resolution of identity (or density fitting) technique.\textsuperscript{S2,S3}

**Photoemission spectrum**

Figure S1 - S40 show the photoemission spectrum (PES) of 40 test molecules. Most the test molecules were from Blase's\textsuperscript{S4} and Marom's\textsuperscript{S5} test set. In addition, polyacene \((n=1-6)\) and two big systems \((C_{60} \text{ and } C_{70})\) were studied as well for interest. Experimental PES were reproduced from literature as reference, if they were applicable. Experimental electron affinity (see clarification of Table S2 for the data source) was broadened with Gaussian expansion with 0.2 eV to plot a peak in the experimental spectrum. Quasi-particle energies from sc\textit{GW} and \(G_0W_0\@PBE\) were obtained from Ref S5 for Marom's test set and used to plot PES for comparison. For orbital energies from DFT, conventional functional (B3LYP and PBE) and LOSC functional (LOSC-B3LYP and LOSC-PBE) were applied for calculation. cc-pVTZ were used as basis set, if not specified. To obtain PES from \textit{GW} and DFT, the orbital energies were used and broadened with Gaussian expansion by 0.2 eV for all the test cases.
Figure S1: Photoemission spectrum of anthracene. Experimental spectrum was obtained from Ref S6

Figure S2: Photoemission spectrum of benzothiadiazole. Experimental spectrum was obtained from Ref S7
Figure S3: Photoemission spectrum of benzothiazole. Experimental spectrum was obtained from Ref S8.

Figure S4: Photoemission spectrum of C$_{60}$. Experimental spectrum was obtained from Ref S9.
Figure S5: Photoemission spectrum of fluorene. Experimental spectrum was obtained from Ref S10

Figure S6: Photoemission spectrum of H$_2$P. Experimental spectrum was obtained from Ref S11
Figure S7: Photoemission spectrum of H$_2$PC. Experimental spectrum was obtained from Ref S12

Figure S8: Photoemission spectrum of H$_2$TPP. Experimental spectrum was obtained from Ref S13
Figure S9: Photoemission spectrum of pentacene. Experimental spectrum was obtained from Ref S14.

Figure S10: Photoemission spectrum of PTCDA. Experimental spectrum was obtained from Ref S15.
Figure S11: Photoemission spectrum of thiadiazole. Experimental spectrum was obtained from Ref S16

Figure S12: Photoemission spectrum of thiphene. Experimental spectrum was obtained from Ref S17
Figure S13: Photoemission spectrum of benzoquinone. Experimental spectrum was obtained from Ref S18.

Figure S14: Photoemission spectrum of Cl₄-isobenzofuranedione.
Figure S15: Photoemission spectrum of dichlone. Experimental spectrum was obtained from Ref S19

Figure S16: Photoemission spectrum of F₄-benzoquinone. Experimental spectrum was obtained from Ref S18
Figure S17: Photoemission spectrum of maleic anhydride. Experimental spectrum was obtained from Ref S5

Figure S18: Photoemission spectrum of nitrobenzene. Experimental spectrum was obtained from Ref S20
Figure S19: Photoemission spectrum of phenazine. Experimental spectrum was obtained from Ref S21

Figure S20: Photoemission spectrum of phthalimide. Experimental spectrum was obtained from Ref S22
Figure S21: Photoemission spectrum of TCNE. Experimental spectrum was obtained from Ref S23

Figure S22: Photoemission spectrum of benzonitrile. Experimental spectrum was obtained from Ref S19
Figure S23: Photoemission spectrum of Cl₄-benzoquinone. Experimental spectrum was obtained from Ref S24.

Figure S24: Photoemission spectrum of dinitrobenzonitrile.
Figure S25: Photoemission spectrum of F_4-benzenedicarbonitrile. Experimental spectrum was obtained from Ref S25

Figure S26: Photoemission spectrum of fumaronitrile. Experimental spectrum was obtained from Ref S26
Figure S27: Photoemission spectrum of mDCNB. Experimental spectrum was obtained from Ref S25

Figure S28: Photoemission spectrum of NDCA. Experimental spectrum was obtained from Ref S27
Figure S29: Photoemission spectrum of nitrobenzonitrile.

Figure S30: Photoemission spectrum of phthalic anhydride. Experimental spectrum was obtained from Ref S22.
Figure S31: Photoemission spectrum of TCNQ. Experimental spectrum was obtained from Ref S23.

Figure S32: Photoemission spectrum of acridine. Experimental spectrum was obtained from Ref S21.
Figure S33: Photoemission spectrum of azulene. Experimental spectrum was obtained from Ref S28.

Figure S34: Photoemission spectrum of bodipy.
Figure S35: Photoemission spectrum of naphthalenedione. Experimental spectrum was obtained from Ref S29

Figure S36: Photoemission spectrum of C\textsubscript{70}. Experimental spectrum was obtained from Ref S30
Figure S37: Photoemission spectrum of benzene. Experimental spectrum was obtained from Ref S31

Figure S38: Photoemission spectrum of naphthalene. Experimental quasi-particle energies were obtained from Ref S6 and used to broaden the spectrum by Gaussian expansion with 0.2 eV.
Figure S39: Photoemission spectrum of tetracene. Experimental quasi-particle energies were obtained from Ref S6 and used to broaden the spectrum by Gaussian expansion with 0.2 eV.

Figure S40: Photoemission spectrum of hexacene. Experimental spectrum was obtained from Ref S32.
**Quasi-particle energy**

Table S1 and S2 show the detailed HOMO and LUMO energies for 40 molecules from density functional approximations (DFAs), LOSC-DFAs, self-consistent GW (scGW), $G_0W_0@$PBE and $\Delta$SCF methods. Most of the test molecules are selected from Blase’s$^{S4}$ and Marom’s$^{S5}$ test set, if not specified. Geometries of Blase’s test set are provided by Blase,$^{S4}$ and geometries of Marom’s test set can be found in Ref S5.

Table S3 shows the valence orbital energies from DFAs, LOSC-DFAs and $\Delta$SCF methods. Test molecules includes polyacene ($n = 1 - 6$) and other three small molecules. Geometries of polyacene ($n = 1 - 6$) were optimized from B3LYP/6-31g* with Gaussian 09 package,$^{S33}$ and attached at the end of SI. Other three geometries are obtained from Ref S34. The basis set used for DFT calculation is cc-pVTZ, if not specified. The fitting basis for LOSC is aug-cc-pVTZ.
Table S1: Comparison of (negative) HOMO energies (in eV) obtained from DFAs, LOSC-DFAs, self-consistent \(GW\) (sc\(GW\)), \(G_0W_0\@PBE\), and \(\Delta\)SCF (PBE and LOSC-PBE) methods with the experimental ionization potential.

| Molecule               | Exp\(^d\) | sc\(GW\)\(^d\) | \(G_0W_0\)\(^f\) | \(\Delta\)PBE | \(\Delta\)LOSCE\(_{\text{PBE}}\) | LDA | PBE | PBE | B3LYP | B3LYP | LDA | LDA | LDA | LDA |
|------------------------|-----------|----------------|-----------------|---------------|---------------------|-----|-----|-----|-------|-------|-----|-----|-----|-----|
| Anthracene\(^d\)      | 7.40       | 6.77           | 7.04            | 7.09          | 7.47                | 5.16 | 4.94 | 5.51 | 7.62  | 7.40  | 7.30 |
| Benzothiadiazole       | 9.00       | NA             | 8.73            | 8.86          | 6.36                | 6.13 | 6.85 | 6.87 | 8.77  | 8.54  | 8.75 |
| Benzothiazole          | 8.80       | NA             | 8.50            | 8.80          | 6.17                | 5.96 | 6.69 | 6.77 | 8.84  | 8.63  | 8.63 |
| C\(_60\)\(^a\)        | 7.60       | NA             | NA              | NA            | 5.92                | 5.66 | 6.18 | 7.98 | 7.76  | 7.86  |
| Fluorene               | 7.90       | NA             | 7.64            | 8.08          | 5.62                | 5.41 | 6.04 | 8.33 | 8.10  | 7.93  |
| H\(_2\)P               | 6.90       | NA             | 6.75            | 6.78          | 5.22                | 4.98 | 5.48 | 7.37 | 7.23  | 7.05  |
| H\(_2\)PC\(^a\)       | 6.40       | NA             | 6.27            | 6.11          | 5.07                | 4.84 | 5.11 | 6.32 | 6.10  | 6.13  |
| H\(_2\)TPP\(^a\)      | 6.40       | NA             | 6.16            | 6.55          | 4.84                | 4.63 | 5.12 | 6.64 | 6.43  | 6.60  |
| Pentacene\(^d\)       | 6.60       | NA             | 6.16            | 6.69          | 4.63                | 4.41 | 4.87 | 6.75 | 6.52  | 6.42  |
| PTCDA                  | 8.20       | NA             | 7.86            | 8.59          | 6.40                | 6.13 | 6.68 | 8.94 | 8.63  | 8.41  |
| Thiadiazole            | 10.10      | NA             | 10.13           | 10.13         | 7.10                | 6.90 | 7.73 | 9.63 | 9.44  | 9.75  |
| thiophene              | 8.85       | NA             | 8.82            | 8.77          | 5.98                | 5.78 | 6.58 | 8.46 | 8.27  | 8.56  |
| Benzoquinone           | 10.03      | 10.22          | 9.41            | 9.21          | 10.75               | 6.43 | 6.25 | 7.67 | 11.00 | 10.80 | 11.01 |
| Cl\(_2\)-isobenzofuranedione | 10.80          | 9.43           | 9.36            | 9.36          | 10.38               | 7.27 | 7.04 | 7.94 | 10.12 | 9.88  | 10.04 |
| Dichlorone             | 9.59       | 9.26           | 9.22            | 8.94          | 10.22               | 6.73 | 6.52 | 7.64 | 9.57  | 9.33  | 9.55  |
| F\(_6\)-benzoquinone  | 10.83      | 10.65          | 10.27           | 10.03         | 10.86               | 7.52 | 7.23 | 8.39 | 10.08 | 9.80  | 10.48 |
| Maleic anhydride       | 11.09      | 11.26          | 10.46           | 10.36         | 11.82               | 7.25 | 7.02 | 8.45 | 11.85 | 11.61 | 11.94 |
| Nitrobenzene           | 9.93       | 9.54           | 9.68            | 9.65          | 10.73               | 6.95 | 6.70 | 7.87 | 9.77  | 9.67  | 9.81  |
| Phenazine              | 8.38       | 7.74           | 7.92            | 7.90          | 8.39                | 5.84 | 5.66 | 6.39 | 8.41  | 8.10  | 8.25  |
| Phthalimide            | 9.84       | 9.45           | 9.37            | 9.24          | 10.76               | 6.48 | 6.25 | 7.66 | 9.68  | 9.51  | 9.69  |
| TCNE                   | 11.78      | 11.36          | 11.19           | 11.15         | 12.50               | 8.83 | 8.55 | 9.42 | 12.54 | 12.30 | 12.30 |
| Benzonitrile           | 9.75       | 9.29           | 9.34            | 9.53          | 10.11               | 7.04 | 6.81 | 7.58 | 9.80  | 9.58  | 9.71  |
| Cl\(_2\)-benzonitrone  | 9.82       | 9.62           | 9.49            | 9.23          | 9.70                | 7.13 | 6.93 | 7.86 | 9.58  | 9.38  | 9.77  |
| Dinitrobenzonitrile    | N/A        | 10.55          | 10.52           | 11.21         | 11.76               | 7.89 | 7.61 | 8.90 | 11.52 | 11.21 | 11.26 |
| F\(_6\)-benzenedicarbonitrile | 10.65          | 10.21          | 9.92            | 10.14         | 10.31               | 7.63 | 7.35 | 8.39 | 9.58  | 9.31  | 10.01 |
| Fumaronitrile          | 11.23      | 10.88          | 10.73           | 10.80         | 11.06               | 8.06 | 7.89 | 8.68 | 10.94 | 10.71 | 10.83 |
| mDCBN                  | 10.40      | 9.80           | 9.80            | 9.86          | 10.46               | 7.60 | 7.35 | 8.14 | 10.38 | 10.13 | 10.24 |
| NDCA                   | 8.98       | 8.45           | 8.62            | 8.69          | 9.56                | 6.67 | 6.42 | 7.10 | 9.43  | 9.18  | 9.09  |
| Nitrobenzonitrile      | 10.40      | 10.02          | 10.02           | 9.94          | 11.60               | 7.45 | 7.19 | 8.37 | 10.51 | 10.28 | 10.53 |
| Phthalic anhydride     | 10.18      | 9.90           | 9.96            | 9.79          | 11.00               | 7.05 | 6.81 | 8.23 | 10.19 | 9.97  | 10.15 |
| TCNQ                   | 9.61       | 8.97           | 9.01            | 9.04          | 8.91                | 7.27 | 7.01 | 7.63 | 8.87  | 8.57  | 8.93  |
Table S1. (Continued.)

| Molecule          | Exp | scGW | G0W0 | ∆PBE | ∆LOSC- | PBE | B3LYP | LOSC- | LOSC- | LOSC- | PBE | B3LYP | LDA | PBE | B3LYP | LOSC- | LOSC- | LOSC- | PBE | B3LYP |
|-------------------|-----|------|------|------|--------|-----|-------|-------|-------|-------|-----|-------|-----|-----|-------|-------|-------|-------|-----|-------|
| Acridine          | 7.99| 7.30 | 7.52 | 7.52 | 8.06   | 5.62| 5.38  | 5.99  | 8.05  | 7.85  | 7.81|       |     |     |       |       |       |       |     |       |
| Azulene           | 7.43| 6.79 | 7.14 | 7.37 | 7.46   | 5.15| 4.92  | 5.52  | 7.63  | 7.40  | 7.34|       |     |     |       |       |       |       |     |       |
| Bodipy            | N/A | 7.48 | 7.83 | 8.04 | 7.76   | 5.97| 5.72  | 6.30  | 8.01  | 7.77  | 8.19|       |     |     |       |       |       |       |     |       |
| Naphthalenedione  | 9.54| 9.21 | 8.99 | 8.75 | 10.39  | 6.29| 6.08  | 7.48  | 9.58  | 9.35  | 9.57|       |     |     |       |       |       |       |     |       |
| C70               | 7.32| N/A  | N/A  | NA   | NA     | 5.91| 5.69  | 6.13  | 7.87  | 7.65  | 7.63|       |     |     |       |       |       |       |     |       |
| Benzene           | 9.24| N/A  | N/A  | 9.25 | 9.25   | 6.50| 6.28  | 7.04  | 8.94  | 8.71  | 8.98|       |     |     |       |       |       |       |     |       |
| Naphthalene       | 8.11| N/A  | N/A  | 7.90 | 8.12   | 5.68| 5.46  | 6.11  | 8.16  | 8.01  | 8.06|       |     |     |       |       |       |       |     |       |
| Tetracene         | 6.97| N/A  | N/A  | 6.55 | 7.03   | 4.87| 4.64  | 5.16  | 7.20  | 7.00  | 6.89|       |     |     |       |       |       |       |     |       |
| Hexacene          | 6.36| N/A  | N/A  | 5.87 | 6.23   | 4.50| 4.26  | 4.73  | 6.62  | 6.40  | 6.30|       |     |     |       |       |       |       |     |       |
| MAE               | -0.43| -0.51| -0.42| 0.20 | -2.58  | -2.81| -2.00 | 0.04  | -0.18 | -0.05 |    |     |     |     |       |       |       |     |       |
| MSE               |     | -0.43| -0.51| -0.42| 0.20   | -2.58| -2.81 | -2.00 | 0.04  | -0.18 | -0.05|     |     |     |       |       |       |     |       |

a cc-pVDZ basis set used for DFT calculation.
b 6-31G basis set was used for DFT calculation. Molecular geometry was obtained from Ref S35.
c Ionization energy was read out from the experimental spectrum shown in Ref S30.
d Geometry was optimized from B3LYP/6-31G* with Gaussian 09 package.\textsuperscript{33}
e Ref S1
f Ref S4 and S5, if not specified.
Table S2: Comparison of (negative) LUMO energies (in eV) obtained from DFAs, LOSC-DFAs, self-consistent GW (scGW), $G_0W_0$@PBE, and $\Delta$SCF (PBE and LOSC-PBE) methods with the experimental electron affinity.

| Molecule                  | Exp | scGW | $G_0W_0$ | $\Delta$PBE | $\Delta$LOS-SCF | LDA PBE | B3LYP | LOSC-PBE | LOSC-B3LYP |
|---------------------------|-----|------|---------|-------------|-----------------|--------|-------|----------|------------|
| Anthracene$^d$            | 0.60 | N/A  | N/A     | 0.50        | 0.29            | 2.92   | 2.68  | 2.09     | 0.87       | 0.62       | 0.48       |
| Benzothiadiazole          | N/A | 0.86 | 0.98    | 0.72        | 0.65            | 3.48   | 3.25  | 2.70     | 1.31       | 1.08       | 1.03       |
| Benzothiazole             | N/A | N/A  | N/A     | -0.37       | -0.54           | 2.32   | 2.09  | 1.41     | -0.12      | -0.37      | -0.49      |
| C$_{60}^a$                | 2.70 | N/A  | N/A     | NA          | NA              | 4.34   | 4.07  | 3.56     | 2.61       | 2.30       | 2.14       |
| Fluorene                  | N/A | N/A  | N/A     | -0.30       | -0.45           | 2.07   | 1.83  | 1.19     | 0.02       | -0.29      | -0.43      |
| H$_2$P                    | N/A | N/A  | N/A     | 1.31        | 1.74            | 3.29   | 3.04  | 2.60     | 1.89       | 1.71       | 1.37       |
| H$_2$PC$^a$               | N/A | N/A  | N/A     | 1.92        | 1.83            | 3.65   | 3.41  | 2.97     | 2.16       | 1.92       | 1.65       |
| H$_2$TPP$^a$              | 1.72 | N/A  | N/A     | 1.33        | 1.17            | 3.03   | 2.82  | 2.37     | 1.58       | 1.32       | 1.16       |
| Pentacened$^d$            | N/A | N/A  | N/A     | 1.50        | 1.24            | 3.55   | 3.31  | 2.80     | 1.59       | 1.38       | 1.47       |
| PTCDA                     | N/A | N/A  | N/A     | 2.90        | 2.63            | 4.90   | 4.60  | 4.18     | 3.02       | 2.69       | 2.71       |
| Thiadiazole               | N/A | N/A  | N/A     | -0.46       | -0.47           | 2.88   | 2.66  | 1.99     | 0.59       | 0.37       | 0.18       |
| thiophene                 | N/A | N/A  | N/A     | -1.48       | -1.48           | 1.57   | 1.36  | 0.68     | -0.55      | -0.76      | -0.99      |
| Benzoquinone              | 1.88 | 2.13 | 2.27    | 1.68        | 1.67            | 4.76   | 4.48  | 3.81     | 2.93       | 2.65       | 2.35       |
| Cl$_2$-isobenzofurandione | 1.96 | 2.32 | 2.25    | 1.70        | 1.54            | 4.28   | 3.99  | 3.43     | 2.14       | 1.87       | 1.74       |
| Dichlorone                | 2.21 | 2.55 | 2.58    | 2.00        | 1.94            | 4.59   | 4.32  | 3.73     | 2.68       | 2.41       | 2.23       |
| F$_2$benzoquinone         | 2.69 | 3.07 | 2.91    | 2.17        | 2.17            | 5.31   | 4.98  | 4.49     | 3.52       | 3.19       | 3.04       |
| Maleic anhydride          | 1.42 | 1.54 | 1.65    | 1.05        | 1.05            | 4.41   | 4.11  | 3.42     | 2.24       | 1.94       | 1.68       |
| Nitrobenzene              | 1.01 | 1.18 | 1.24    | 0.55        | 0.28            | 3.65   | 3.35  | 2.71     | 0.64       | 0.35       | 0.34       |
| Phenazine                 | 1.31 | 1.70 | 1.77    | 1.16        | 1.11            | 3.60   | 3.34  | 2.75     | 1.54       | 1.29       | 1.20       |
| Phthalimide               | 1.02 | 1.17 | 1.26    | 0.69        | 0.58            | 3.49   | 3.20  | 2.56     | 1.50       | 1.22       | 1.04       |
| TCNE                      | 3.17 | 3.80 | 3.78    | 3.13        | 3.22            | 6.03   | 5.74  | 5.22     | 4.08       | 3.78       | 3.70       |
| Benzonitrile              | 0.26 | 0.26 | 0.40    | -0.15       | -0.15           | 2.71   | 2.45  | 1.77     | 0.58       | 0.28       | 0.28       |
| Cl$_2$-benzonitrone       | 2.77 | 3.15 | 3.11    | 2.50        | 2.53            | 5.21   | 4.94  | 4.39     | 3.21       | 2.96       | 3.01       |
| Dinitrobenzonitrile       | 2.16 | 2.53 | 2.46    | 2.12        | 1.36            | 4.79   | 4.47  | 3.88     | 1.86       | 1.54       | 1.60       |
| F$_2$-benzenedicarbonitrile| 1.89 | 2.38 | 2.18    | 1.59        | 1.46            | 4.36   | 4.05  | 3.57     | 2.29       | 2.09       | 2.11       |
| Fumaronitrile             | 1.25 | 1.49 | 1.68    | 1.11        | 1.11            | 4.31   | 4.04  | 3.37     | 2.07       | 1.79       | 1.61       |
| mDCBN                     | 0.91 | 1.16 | 1.27    | 0.77        | 0.69            | 3.50   | 3.23  | 2.58     | 1.55       | 1.28       | 1.07       |
| NDCA                      | N/A | 1.85 | 1.91    | 1.40        | 1.10            | 3.87   | 3.59  | 3.01     | 1.90       | 1.62       | 1.43       |
| Nitrobenzonitrile         | 1.71 | 2.02 | 2.01    | 1.49        | 1.14            | 4.33   | 4.03  | 3.44     | 1.54       | 1.21       | 1.27       |
| Phthalic anhydride        | 1.26 | 1.44 | 1.52    | 0.96        | 0.87            | 3.81   | 3.52  | 2.87     | 1.75       | 1.46       | 1.36       |
| Molecule        | Exp  | scGW  | G_{0W_0} | ∆PBE | ∆LOSC-PBE | LDA PBE | B3LYP PBE | LOSC-PBE | LOSC-PBE | LOSC-B3LYP |
|-----------------|------|-------|-----------|------|-----------|---------|-----------|----------|----------|------------|
| TCNQ            | 2.80 | 4.11  | 4.02      | 3.41 | 3.77      | 5.75    | 5.47      | 5.08     | 4.31     | 4.05       | 3.89       |
| Acridine        | 0.90 | 1.23  | 1.33      | 0.80 | 0.72      | 3.18    | 2.93      | 2.33     | 1.13     | 0.87       | 0.75       |
| Azulene         | 0.75 | 1.07  | 1.10      | 0.43 | 0.60      | 3.07    | 2.82      | 2.20     | 1.17     | 0.92       | 0.78       |
| Bodipy          | N/A  | 2.18  | 2.13      | 1.43 | 1.87      | 3.96    | 3.70      | 3.20     | 2.25     | 2.00       | 1.77       |
| Naphthalenedione| 1.81 | 2.05  | 2.18      | 1.62 | 1.56      | 4.38    | 4.10      | 3.45     | 2.43     | 2.14       | 1.89       |
| C_{70}          | 2.76 | N/A   | N/A       | 2.45 | 2.31      | 4.18    | 3.95      | 3.46     | 2.54     | 2.36       | 2.15       |
| Benzene         | -1.12| N/A   | N/A       | -1.63| -1.64     | 1.38    | 1.13      | 0.39     | -0.73    | -0.97      | -1.26      |
| Naphthalene     | -0.20| N/A   | N/A       | -0.36| -0.40     | 2.25    | 2.00      | 1.33     | 0.16     | -0.09      | -0.31      |
| Tetracene       | 1.06 | N/A   | N/A       | 1.08 | 0.85      | 3.22    | 2.96      | 2.41     | 1.26     | 1.00       | 0.92       |
| Hexacene        | 1.47 | N/A   | N/A       | 1.82 | 1.88      | 3.67    | 3.42      | 2.91     | 1.76     | 1.48       | 1.45       |
| MAE             | 0.34 | 0.37  | 0.26      | 0.38 | 0.26      | 2.43    | 2.16      | 1.57     | 0.48     | 0.33       | 0.29       |
| MSE             | 0.34 | 0.37  | -0.19     | -0.28| 2.43      | 2.16    | 1.57      | 0.39     | 0.11     | -0.02      |

a cc-pVDZ basise set was used for DFT calculation.
b 6-31G basise set was used for DFT calculation. Molecular geometry was obtained form Ref S35.
c Ref S36
d Geometry was optimized from B3LYP/6-31G* with Gaussian 09 package. S33
e Ref S1
f Ref S4 and S5, if not specified.
Table S3: Occupied orbital energies (in eV) obtained from DFAs, LOSC-DFAs and \( \Delta \text{SCF} \) methods (B3LYP and LOSC-B3LYP) compared with the experimental reference.

| Molecule   | State | Exp* | \( \Delta \text{B3LYP} \) | \( \Delta \text{LOSC-B3LYP} \) | LDA | PBE | BLYP | B3LYP | LOSC-LDA | LOSC-PBE | LOSC-BLYP | LOSC-B3LYP |
|------------|-------|------|-----------------|-------------------|-----|-----|-----|-----|---------|---------|---------|---------|
| Benzene    | \( E_{1g} \) | 9.24 | 9.07 | 9.06 | 6.50 | 6.28 | 6.09 | 7.04 | 8.94 | 8.71 | 8.51 | 8.98 |
|            | \( E_{1g} \) | 9.24 | 9.08 | 9.07 | 6.50 | 6.28 | 6.09 | 7.04 | 8.93 | 8.70 | 8.50 | 8.96 |
|            | \( A_{2u} \) | 12.25 | NA | NA | 8.26 | 8.18 | 8.12 | 9.48 | 11.41 | 11.33 | 11.54 | 12.12 |
| MAE        |       | 0.17 | 0.18 | 3.16 | 3.33 | 3.48 | 2.39 | 0.48 | 0.66 | 0.73 | 0.22 |
| Naphthalene| \( A_{1u} \) | 8.15 | 7.71 | 8.00 | 5.68 | 5.46 | 5.26 | 6.11 | 8.16 | 8.01 | 7.71 | 8.06 |
|            | \( B_{1u} \) | 8.87 | 8.47 | 9.03 | 6.40 | 6.18 | 5.97 | 6.86 | 9.37 | 9.20 | 8.84 | 9.12 |
|            | \( B_{2g} \) | 10.08 | 9.44 | 9.73 | 7.34 | 7.12 | 6.91 | 7.98 | 9.84 | 9.73 | 9.37 | 10.03 |
|            | \( B_{3g} \) | 10.83 | 10.32 | 11.15 | 7.98 | 7.87 | 7.81 | 9.13 | 11.25 | 11.17 | 11.12 | 11.54 |
| MAE        |       | 0.50 | 0.25 | 2.63 | 2.82 | 3.00 | 1.97 | 0.29 | 0.29 | 0.37 | 0.27 |
|Anthracene  | \( B_{2g} \) | 7.41 | 6.89 | 7.30 | 5.19 | 4.97 | 4.76 | 5.54 | 7.66 | 7.44 | 7.23 | 7.36 |
|            | \( B_{3g} \) | 8.54 | 8.10 | 8.90 | 6.36 | 6.13 | 5.92 | 6.76 | 9.28 | 9.11 | 8.87 | 9.01 |
|            | \( A_{uu} \) | 9.19 | 8.38 | 9.24 | 6.68 | 6.45 | 6.24 | 7.22 | 9.52 | 9.36 | 9.15 | 9.43 |
|            | \( B_{1u} \) | 10.18 | NA | NA | 7.68 | 7.45 | 7.24 | 8.35 | 10.36 | 10.20 | 9.99 | 10.52 |
|            | \( B_{3g} \) | 10.28 | 9.52 | 10.52 | 7.83 | 7.60 | 7.38 | 8.50 | 10.84 | 10.67 | 10.44 | 10.86 |
| MAE        |       | 0.63 | 0.19 | 2.37 | 2.60 | 2.81 | 1.84 | 0.41 | 0.24 | 0.18 | 0.33 |
|Teracene    | \( A_{uu} \) | 6.97 | 6.35 | 6.86 | 4.87 | 4.64 | 4.44 | 5.16 | 7.20 | 7.00 | 6.86 | 6.89 |
|            | \( AB_{2u} \) | 8.41 | 7.61 | 8.54 | 6.16 | 5.93 | 5.72 | 6.64 | 8.82 | 8.62 | 8.50 | 8.60 |
|            | \( B_{1u} \) | 8.41 | 7.84 | 8.81 | 6.35 | 6.11 | 5.89 | 6.71 | 9.27 | 9.08 | 8.83 | 8.80 |
|            | \( A_{uu} \) | 9.56 | 8.66 | 9.70 | 7.19 | 6.95 | 6.74 | 7.80 | 9.93 | 9.76 | 9.61 | 9.90 |
|            | \( B_{3g} \) | 9.70 | 8.92 | 10.08 | 7.48 | 7.25 | 7.02 | 8.08 | 10.50 | 10.30 | 10.06 | 10.32 |
|            | \( B_{2g} \) | 10.25 | 9.46 | 9.93 | 7.85 | 7.62 | 7.40 | 8.54 | 10.41 | 10.22 | 10.04 | 10.54 |
| MAE        |       | 0.74 | 0.25 | 2.23 | 2.47 | 2.68 | 1.73 | 0.47 | 0.29 | 0.21 | 0.32 |
|Pentacene   | \( B_{2g} \) | 6.61 | 5.96 | 6.47 | 4.66 | 4.42 | 4.22 | 4.90 | 6.78 | 6.59 | 6.42 | 6.46 |
|            | \( A_{uu} \) | 7.92 | 7.04 | 7.88 | 5.77 | 5.54 | 5.33 | 6.19 | 8.26 | 8.00 | 7.83 | 8.16 |
|            | \( B_{1u} \) | 8.32 | 7.64 | 8.79 | 6.34 | 6.10 | 5.87 | 6.68 | 9.24 | 9.04 | 8.80 | 8.97 |
|            | \( B_{2g} \) | 9.01 | 8.02 | 9.20 | 6.74 | 6.51 | 6.29 | 7.29 | 9.49 | 9.28 | 9.15 | 9.16 |
|            | \( B_{1u} \) | 9.39 | 8.50 | 9.79 | 7.24 | 7.00 | 6.78 | 7.78 | 10.21 | 9.98 | 9.77 | 10.14 |
|            | \( A_{uu} \) | 9.80 | 8.79 | 10.04 | 7.48 | 7.24 | 7.02 | 8.12 | 10.11 | 9.85 | 9.70 | 10.11 |
|            | \( B_{2g} \) | 10.23 | NA | NA | 7.88 | 7.72 | 7.50 | 8.65 | 11.48 | 10.46 | 10.28 | 10.67 |
| Molecule | State | Exp | ∆B3LYP | ∆LOSC-B3LYP | LDA | PBE | B3LYP | LOSC-LDA | PBE | B3LYP | LOSC-B3LYP | MAE |
|----------|-------|-----|--------|-------------|-----|-----|-------|----------|-----|------|------------|-----|
| Hexacene | $A_u$  | 6.36 | 5.67   | 5.97       | 4.50 | 4.26 | 4.06  | 4.73     | 6.62 | 6.40 | 6.18       | 6.30|
|          | $B_{2g}$ | 7.35 | 6.60   | 7.41       | 5.48 | 5.24 | 5.03  | 5.84     | 7.95 | 7.77 | 7.56       | 7.80|
|          | $B_{3u}$ | 8.12 | 7.49   | 8.36       | 6.33 | 6.09 | 5.86  | 6.66     | 9.26 | 9.06 | 8.78       | 8.96|
|          | $A_u$  | 8.56 | 7.50   | 8.29       | 6.37 | 6.14 | 5.92  | 6.87     | 9.09 | 8.54 | 8.35       | 8.68|
|          | $B_{2g}$ | 9.36 | 8.18   | 9.38       | 7.07 | 6.83 | 6.60  | 7.57     | 10.01| 9.79 | 9.55       | 9.91|
|          | $B_{3g}$ | 9.36 | 8.24   | 8.83       | 7.11 | 6.87 | 6.65  | 7.70     | 9.69 | 9.56 | 9.35       | 9.76|
| Thiophene | $A_u$  | 9.95 | 8.83   | 9.43       | 7.66 | 7.43 | 7.20  | 8.32     | 10.42| 9.97 | 9.82       | 10.32|
|          | $B_{2g}$ | 9.95 | 9.14   | 10.62      | 7.88 | 7.55 | 6.60  | 8.66     | 11.51| 11.36| 10.57      | 11.02|
| Ethylene | $B_{3u}$ | 10.68 | 10.53  | 10.53      | 6.92 | 6.73 | 6.55  | 7.62     | 10.63| 10.45| 10.26      | 10.59|
|          | $B_{2g}$ | 12.80 | 12.39  | 12.39      | 8.48 | 8.51 | 8.47  | 9.82     | 11.33| 11.35| 11.31      | 12.10|
|          | $A_u$  | 14.80 | 14.24  | 14.24      | 10.23| 10.14| 10.08 | 11.56    | 13.92| 13.83| 13.78      | 14.52|
|          | $B_{2g}$ | 16.00 | 15.45  | 15.45      | 11.56| 11.49| 11.39 | 12.93    | 14.80| 14.72| 14.61      | 15.50|
|          | $B_{1g}$ | 19.10 | 18.20  | 18.20      | 14.16| 14.22| 14.08 | 15.89    | 17.34| 17.41| 17.27      | 18.44|
|          | $A_u$  | 23.60 | 23.25  | 23.25      | 18.72| 18.79| 18.60 | 20.82    | 23.18| 23.25| 23.06      | 24.40|
| Water    | $B_{1u}$ | 12.62 | 12.60  | 12.60      | 6.99 | 6.83 | 6.77  | 8.49     | 13.11| 12.98| 12.92      | 13.42|
|          | $A_{1g}$ | 14.74 | 14.71  | 14.71      | 9.02 | 8.94 | 8.85  | 10.55    | 15.13| 15.03| 14.94      | 15.41|
|          | $B_{2g}$ | 18.55 | 18.74  | 18.74      | 12.98| 12.90| 12.81 | 14.44    | 18.46| 18.38| 18.28      | 18.83|
Table S3. (Continued.)

| Molecule    | State | Exp<sup>a</sup> | ∆B3LYP | ∆LOSC-B3LYP | LDA | PBE | BLYP | B3LYP | LOSC-LDA | LOSC-PBE | LOSC-BLYP | LOSC-B3LYP |
|-------------|-------|------------------|--------|-------------|-----|-----|------|-------|----------|----------|-----------|-----------|
| MAE Polyacene |       |                  | 0.08   | 5.64        | 5.75 | 5.83 | 4.14 | 0.32  | 0.27     | 0.26     | 0.58      |
| MSE Polyacene |       |                  | -0.73  | -2.33       | -2.55 | -2.76 | -1.79 | 0.53  | 0.35     | 0.29     | 0.36      |
| Total MAE   |       |                  | 0.70   | 3.06        | 3.23 | 3.40 | 2.24 | 0.69  | 0.60     | 0.60     | 0.43      |
| Total MSE   |       |                  | -0.69  | -3.06       | -3.23 | -3.40 | -2.24 | -0.06 | -0.23    | -0.41    | 0.08      |

<sup>a</sup> The experimental data for polyacene (n = 1 - 6) were obtained from Ref S6, other experimental data were obtained from Ref S37.
Excitation energy

Table S4 - S6 show the detailed low-lying excitation energies of 16 molecular test set from different methods. The basis set used for DFT calculation was 6-311++G(3df, 3pd), if not specified. Gaussian 09 package\textsuperscript{S33} was applied to perform TD-DFT calculation, and ccpVTZ were used as basis set. Geometries were obtained from Ref S38. Table S7 - S12 show detailed excitation energies of 4 atoms (Li, Be, Mg and Na) in which Rydberg excited states were concerned. To describe Rydberg states of these 4 atoms, greatly diffused basis set were used to perform the calculation. Here even-tempered basis set was built, with its Gaussian orbital exponents $\alpha$ satisfying $\alpha_i = 2^{i-1}\alpha_1$. Each of the even-tempered basis contains 17s, 15p and 11d functions with the smallest exponents being $\alpha_1 = 0.000976525, 0.000976525, \text{ and } 0.0039062500$, respectively. For excitation calculation from DFT by orbital energies, unrestricted calculation were applied for all test cases.
Table S4: Low-lying vertical excitation energies (in eV) obtained from N-1 system with Hartree Fock (HF), DFAs, LOSC-DFAs, TD-B3LYP, and ∆SCF-B3LYP.

| Molecule       | MO   | Refa | TD-B3LYP | ∆SCF-B3LYP | BLYP | B3LYP | LDA | HF  | LOSC-B3LYP | LOSC-B3LYP | LOSC-LDA |
|----------------|------|------|----------|------------|------|-------|-----|-----|------------|------------|---------|
| Ethene         | 3B1u | 4.50 | 4.05     | 4.38       | 4.61 | 4.43  | 4.90| 3.09| 4.15       | 4.05       | 4.40    |
| Ethene         | 1B1u | 7.80 | 7.38     | 7.09       | 7.46 | 7.75  | 7.27| 6.61| 6.61       | 7.00       | 6.52    |
| Furan          | 3B2  | 4.17 | 3.70     | 3.98       | 4.05 | 3.95  | 4.31| 2.95| 3.74       | 3.71       | 3.88    |
| Furan          | 3A2  | 5.99*| 5.48     | 5.75       | 5.78 | 5.84  | 5.99| 3.99| 5.63       | 5.71       | 5.71    |
| Furan          | 1B2  | 6.32 | 5.94     | 5.78       | 5.73 | 6.11  | 5.60| 5.07| 5.76       | 6.08       | 5.43    |
| Furan          | 1A2  | 6.03*| 5.51     | 5.88       | 6.91 | 7.27  | 6.91| 4.92| 6.86       | 7.15       | 6.69    |
| Benzoquinone   | 3B1g | 2.51 | 1.93     | 2.08       | 1.68 | 2.08  | 1.60| 3.28| 2.08       | 2.36       | 1.99    |
| Benzoquinone   | 3B3u | 5.38*| 5.18     | 5.12       | 4.76 | 5.40  | 4.66| 7.21| 5.36       | 5.81       | 5.28    |
| Benzoquinone   | 1B1g | 2.78 | 2.43     | 2.38       | 1.95 | 2.41  | 1.94| 4.11| 2.30       | 2.64       | 2.30    |
| Benzoquinone   | 3B3u | 5.60 | 5.38     | 5.51       | 4.85 | 5.49  | 4.78| 7.14| 5.14       | 5.45       | 5.89    |
| cyclopentadiene| 3B2  | 3.25 | 2.74     | 3.11       | 3.21 | 3.12  | 3.46| 2.30| 2.82       | 2.82       | 3.06    |
| cyclopentadiene| 3A2  | 5.61*| 5.09     | 5.37       | 5.65 | 5.76  | 5.85| 3.60| 5.49       | 5.59       | 5.67    |
| cyclopentadiene| 1B2  | 5.55 | 4.95     | 4.82       | 4.74 | 5.06  | 4.66| 4.93| 4.29       | 4.70       | 4.22    |
| cyclopentadiene| 1A2  | 5.65*| 5.11     | 5.40       | 6.79 | 7.14  | 6.77| 4.66| 6.38       | 6.75       | 6.44    |
| butadiene      | 3B3u | 3.20 | 2.79     | 3.20       | 3.22 | 3.19  | 3.40| 2.54| 2.76       | 3.06       | 2.90    |
| butadiene      | 3B2  | 6.22*| 5.67     | 5.80       | 5.86 | 6.02  | 6.05| 4.09| 5.53       | 5.96       | 5.68    |
| butadiene      | 1B1u | 6.18 | 5.56     | 5.13       | 4.86 | 5.39  | 4.72| 5.72| 5.08       | 5.74       | 4.80    |
| butadiene      | 1B2  | 6.26*| 5.70     | 6.10       | 6.80 | 7.04  | 6.86| 4.73| 6.81       | 7.27       | 6.78    |
| hexatriene     | 3B3u | 2.40 | 2.12     | 2.52       | 2.49 | 2.51  | 2.62| 1.92| 2.76       | 2.53       | 2.94    |
| hexatriene     | 3A3u | 5.68*| 5.22     | 4.99       | 4.82 | 5.10  | 4.95| 3.55| 5.54       | 5.44       | 5.72    |
| hexatriene     | 1B1u | 5.10 | 4.60     | 4.11       | 3.66 | 4.22  | 3.54| 5.20| 4.02       | 4.70       | 3.97    |
| hexatriene     | 1A1u | 5.71*| 5.24     | 5.79       | 5.58 | 6.05  | 5.60| 3.98| 6.09       | 6.36       | 6.26    |
| octetraene     | 3B3u | 2.20 | 1.71     | 2.10       | 2.05 | 2.11  | 1.97| 1.57| 2.00       | 2.00       | 2.91    |
| octetraene     | 3B2  | 4.66 | 3.96     | 3.47       | 2.96 | 3.52  | 2.86| 4.86| 3.93       | 3.92       | 3.88    |
| cyclopropene   | 3B2  | 4.34 | 3.70     | 4.03       | 4.22 | 4.19  | 4.38| 3.16| 4.49       | 4.34       | 4.69    |
| cyclopropene   | 3B2  | 7.06 | 6.09     | 6.27       | 6.29 | 6.69  | 5.97| 6.20| 6.23       | 6.50       | 6.07    |
| norbornadiene  | 3A2  | 3.72 | 3.10     | 3.54       | 3.62 | 3.71  | 3.73| 3.50| 4.00       | 3.92       | 4.08    |
| norbornadiene  | 1A2  | 5.34 | 4.70     | 4.73       | 4.64 | 4.90  | 4.56| 4.89| 4.82       | 4.87       | 4.77    |
| s-tetrazine    | 3B1u | 1.89 | 1.47     | 1.62       | 1.32 | 1.63  | 1.21| 2.48| 1.28       | 1.72       | 1.22    |
| Molecule      | MO   | Refa | TD-REF | ΔSCF-B3LYP | BLYP | B3LYP | LDA  | HF   | LOSC-B3LYP | LOSC-B3LYP | LOSC-B3LYP | LDA  |
|---------------|------|------|--------|------------|------|-------|------|------|------------|------------|------------|------|
| s-tetrazine   | $^3A_u$ | 3.52 | 3.15   | 3.34       | 2.98 | 3.45  | 2.85 | 4.90 | 2.95       | 3.54       | 2.86       |
| s-tetrazine   | $^1B_u$ | 2.24 | 2.27   | 2.12       | 1.77 | 2.17  | 1.74 | 3.57 | 1.73       | 2.25       | 1.74       |
| s-tetrazine   | $^1A_u$ | 3.48 | 3.54   | N/A        | 3.13 | 3.59  | 3.06 | 4.88 | 3.08       | 3.66       | 3.06       |
| formaldehyde  | $^3A_2$ | 3.50 | 3.10   | 3.19       | 3.37 | 3.17  | 3.38 | 1.17 | 2.94       | 2.73       | 3.08       |
| formaldehyde  | $^1A_2$ | 3.88 | 3.83   | 3.48       | 3.63 | 3.41  | 3.89 | 1.20 | 3.09       | 2.87       | 3.47       |
| acetone       | $^3B_1$ | 4.05 | 3.68   | 3.75       | 3.95 | 3.78  | 4.09 | 1.82 | 3.36       | 3.24       | 3.53       |
| acetone       | $^3B_2$ | 5.87* | 5.71   | 6.20       | 7.95 | 7.47  | 8.38 | 2.81 | 6.23       | 5.99       | 6.78       |
| acetone       | $^1B_1$ | 4.40 | 4.30   | 4.00       | 4.19 | 4.01  | 4.50 | 1.89 | 3.57       | 3.43       | 3.90       |
| acetone       | $^1B_2$ | 5.92* | 5.77   | 6.24       | 8.02 | 7.54  | 8.46 | 2.85 | 6.30       | 6.01       | 6.65       |
| pyridine      | $^3B_1$ | 4.25 | 4.05   | 4.42       | 4.37 | 4.42  | 4.43 | 2.82 | 3.22       | 4.21       | 2.93       |
| pyridine      | $^3A_2$ | 5.28 | 4.96   | N/A        | 4.99 | 4.60  | 5.15 | 3.54 | 3.84       | 4.40       | 3.65       |
| pyridine      | $^3B_1$ | 4.59 | 4.76   | 4.45       | 4.80 | 5.54  | 4.89 | 2.09 | 3.57       | 5.29       | 3.33       |
| pyridazine    | $^3B_1$ | 3.78 | 3.60   | 3.51       | 3.61 | 3.64  | 3.64 | 3.86 | 2.41       | 2.69       | 2.40       |
| pyridazine    | $^1A_2$ | 4.32 | 4.19   | N/A        | 4.25 | 4.25  | 4.26 | 2.59 | 3.03       | 3.28       | 2.99       |
| pyrazine      | $^1B_u$ | 3.95 | 3.93   | 3.81       | 3.53 | 3.90  | 3.52 | 5.12 | 3.57       | 3.55       | 3.55       |
| pyrazine      | $^1A_u$ | 4.81 | 4.69   | N/A        | 4.39 | 4.76  | 4.34 | 5.56 | 4.35       | 4.35       | 4.30       |
| pyrimidine    | $^1B_1$ | 4.55 | 4.25   | 4.11       | 3.97 | 4.17  | 4.01 | 3.40 | 3.72       | 3.77       | 3.75       |
| pyrimidine    | $^1A_2$ | 4.91 | 4.60   | N/A        | 4.37 | 4.59  | 4.40 | 3.95 | 4.19       | 4.23       | 4.19       |

| MAE | 0.38 | 0.35 | 0.53 | 0.42 | 0.58 | 1.35 | 0.63 | 0.49 | 0.67 |
| MSE | -0.37 | -0.31 | -0.22 | -0.01 | -0.16 | -0.83 | -0.44 | -0.19 | -0.42 |

*a Reference data labeled with an asterisk are obtained from CC2/aug-cc-pVTZ calculation with TURBOMOLE package, other reference values were obtained from Ref S40.
Table S5: Low-lying vertical excitation energies (in eV) obtained from N+1 system with Hartree Fock (HF), DFAs, LOSC-DFAs, TD-B3LYP and ∆SCF-B3LYP.

| Molecule       | MO | Refa | TD-B3LYP | ∆SCF-B3LYP | BLYP | B3LYP | LDA | HF | LOSC-BLYP | LOSC-B3LYP | LOSC-LDA |
|----------------|----|------|----------|-------------|------|-------|-----|----|-----------|-----------|---------|
| Ethene         | 1B_u | 7.80 | 7.38 | 7.09 | 4.89 | 5.61 | 5.07 | 7.63 | 7.78 | 7.92 | 7.92 |
| Ethene         | 3B_u | 4.50 | 4.05 | 4.38 | 4.86 | 5.59 | 5.02 | 7.65 | 7.75 | 7.88 | 7.89 |
| Furan          | 1B_u | 6.32 | 5.94 | 5.78 | 3.96 | 4.67 | 4.15 | 6.90 | 6.15 | 6.37 | 6.38 |
| Furan          | 3B_u | 4.17 | 3.70 | 3.98 | 3.95 | 4.65 | 4.12 | 6.90 | 6.22 | 6.33 | 6.34 |
| Benzoquinone   | 1B_u | 2.78 | 2.43 | 2.38 | 1.81 | 2.39 | 1.79 | 4.71 | 4.67 | 4.55 | 4.51 |
| Benzoquinone   | 3B_u | 2.51 | 1.93 | 2.08 | 1.54 | 2.06 | 1.45 | 2.71 | 4.34 | 4.20 | 4.15 |
| cyclopentadiene| 1B_u | 5.55 | 4.95 | 4.82 | 3.64 | 4.32 | 3.75 | 6.63 | 5.74 | 5.99 | 5.75 |
| cyclopentadiene| 3B_u | 3.25 | 2.74 | 3.11 | 3.63 | 4.31 | 3.66 | 6.63 | 5.73 | 5.98 | 5.67 |
| butadiene      | 1B_u | 6.18 | 5.56 | 5.13 | 3.92 | 4.71 | 3.95 | 6.68 | 6.36 | 5.74 | 6.14 |
| butadiene      | 3B_u | 3.20 | 2.79 | 3.20 | 3.52 | 3.27 | 3.50 | 6.67 | 5.81 | 3.88 | 5.56 |
| hexatriene     | 1B_u | 5.10 | 4.60 | 4.11 | 3.25 | 3.88 | 3.22 | 6.20 | 4.13 | 4.71 | 4.28 |
| hexatriene     | 3B_u | 2.40 | 2.12 | 2.52 | 2.45 | 2.55 | 2.56 | 6.17 | 3.24 | 2.92 | 3.40 |
| octetraene     | 1B_u | 4.66 | 3.96 | 3.47 | 2.72 | 3.30 | 2.68 | 5.87 | 4.12 | 3.83 | 3.99 |
| octetraene     | 3B_u | 2.20 | 1.71 | 2.10 | 2.04 | 2.13 | 2.12 | 1.82 | 3.17 | 2.61 | 3.26 |
| cyclopropene   | 1B_u | 7.06 | 6.09 | 6.27 | 4.42 | 5.18 | 4.49 | 7.83 | 6.74 | 7.04 | 6.74 |
| cyclopropene   | 3B_u | 4.34 | 3.70 | 4.03 | 4.40 | 5.16 | 4.45 | 7.81 | 6.72 | 7.02 | 6.71 |
| norbornadiene  | 1A_2 | 5.34 | 4.70 | 4.73 | 3.76 | 4.51 | 3.77 | 6.99 | 6.56 | 6.72 | 6.42 |
| norbornadiene  | 3A_2 | 3.72 | 3.10 | 3.54 | 3.75 | 4.50 | 3.66 | 6.98 | 6.55 | 6.72 | 6.33 |
| s-tetrazine    | 1B_u | 2.24 | 2.27 | 2.12 | 1.74 | 2.09 | 1.74 | 3.11 | 2.96 | 2.86 | 3.00 |
| s-tetrazine    | 3B_u | 1.89 | 1.47 | 1.62 | 1.37 | 1.61 | 1.30 | 1.90 | 2.64 | 2.60 | 2.57 |
| formaldehyde   | 1A_2 | 3.88 | 3.83 | 3.48 | 3.34 | 3.67 | 3.28 | 5.65 | 6.18 | 4.78 | 5.84 |
| formaldehyde   | 3A_2 | 3.50 | 3.10 | 3.19 | 3.19 | 3.29 | 3.02 | 4.82 | 5.99 | 4.35 | 5.55 |
| acetone        | 1B_1 | 4.40 | 4.30 | 4.00 | 3.97 | 5.08 | N/A | 8.79 | 7.50 | 7.77 | N/A |
| acetone        | 3B_1 | 4.05 | 3.68 | 3.75 | 3.95 | 5.07 | N/A | 8.80 | 7.32 | 7.75 | N/A |
| pyridine       | 1B_1 | 4.59 | 4.76 | 4.45 | 4.12 | 5.36 | 4.00 | 7.70 | 7.67 | 8.16 | 7.29 |
| pyridine       | 3B_1 | 4.25 | 4.05 | 4.42 | 4.04 | 5.29 | 3.85 | 7.69 | 7.61 | 8.09 | 7.16 |
| pyridazine     | 1B_1 | 3.78 | 3.60 | 3.51 | 2.93 | 3.40 | 2.83 | 6.27 | 4.96 | 4.40 | 4.64 |
| pyrazine       | 1B_u | 3.95 | 3.93 | 3.81 | 3.28 | 3.74 | 3.27 | 5.27 | 6.40 | 5.58 | 5.57 |
Table S5. (Continued.)

| Molecule | MO  | Ref<sup>a</sup> | TD-<sub>B3LYP</sub> | ΔSCF-<sub>B3LYP</sub> | BLYP | B3LYP | LDA | HF  | LOSC-<sub>BLYP</sub> | LOSC-<sub>B3LYP</sub> | LOSC-<sub>LDA</sub> |
|----------|-----|----------------|----------------------|------------------------|------|-------|-----|-----|---------------------|---------------------|----------------------|
| pyrimidine | 1<sup>B</sup><sub>t</sub> | 4.55 | 4.25 | 4.11 | 3.64 | 4.07 | 3.58 | 7.81 | 6.82 | 5.75 | 6.57 |
| MAE      | 0.41 | 0.40 | 0.91 | 0.78 | 0.98 | 2.05 | 1.72 | 1.51 | 1.47 |
| MSE      | -0.40 | -0.38 | -0.83 | -0.23 | -0.87 | 2.01 | 1.58 | 1.39 | 1.33 |

<sup>a</sup> Reference values were obtained from Ref S40.
Table S6: Errors (in eV) of the vertical excitation energies from $(N + 1)$-system with HF, DFAs, LOSC-DFAs, TD-B3LYP, and ΔSCF-DFT. T1 stands for triplet HOMO to LUMO excitation, and S1 stands for singlet HOMO to LUMO excitation.

| Method          | T1  | S1  | Total |
|-----------------|-----|-----|-------|
|                 | MAE | MSE | MAE   | MSE   | MAE  | MSE  |
| HF              | 2.56| 2.51| 1.64  | 1.62  | 2.05 | 2.01 |
| BLYP            | 0.28| -0.10| 1.43  | -1.43 | 0.91 | -0.83|
| B3LYP           | 0.58| 0.42| 0.94  | -0.76 | 0.78 | -0.23|
| LDA             | 0.35| -0.10| 1.48  | -1.48 | 0.98 | -0.87|
| LOSC-BLYP       | 2.25| 2.25| 1.29  | 1.04  | 1.72 | 1.58 |
| LOSC-B3LYP      | 2.03| 2.03| 1.08  | 0.87  | 1.51 | 1.39 |
| LOSC-LDA        | 2.05| 2.05| 1.00  | 0.75  | 1.47 | 1.33 |
| TD-B3LYP        | 0.45| -0.45| 0.38  | -0.35 | 0.41 | -0.40|
| ΔSCF-B3LYP      | 0.20| -0.16| 0.56  | -0.56 | 0.40 | -0.38|
Table S7: Doublet excitation energy (in eV) of atom Li. Experimental data were obtained from Ref S41.

| AO | Exp | LDA | BLYP | B3LYP | LOSC-LDA | LOSC-BLYP | LOSC-B3LYP |
|----|-----|-----|------|-------|----------|-----------|------------|
| 2p | 1.85| 1.95| 2.07 | 2.06  | 1.96     | 2.18      | 2.08       |
| 3s | 3.37| 4.30| 4.80 | 4.56  | 2.78     | 3.53      | 3.46       |
| 3p | 3.83| 4.72| 5.33 | 5.07  | 3.15     | 4.02      | 3.90       |
| 3d | 3.88| 4.98| 5.56 | 5.27  | 3.43     | 4.29      | 4.15       |
| 4s | 4.34| 5.40| 6.23 | 5.84  | 3.31     | 4.30      | 4.24       |
| 4p | 4.52| 5.56| 6.42 | 6.03  | 3.43     | 4.45      | 4.43       |
| 4d | 4.54| 5.66| 6.52 | 6.12  | 3.58     | 4.55      | 4.53       |
| 5s | 4.75| 5.85| 6.81 | 6.19  | 3.54     | 4.66      | 4.39       |
| 5p | 4.84| 5.92| 6.92 | 6.49  | 3.60     | 4.78      | 4.72       |
| 5d | 4.85| -   | 7.04 | 6.62  | -        | 5.00      | 4.98       |
| 6s | 4.96| 6.07| 7.11 | 6.62  | 3.61     | 4.74      | 4.69       |
| 6p | 5.01| 6.12| 7.12 | 6.68  | 3.67     | 4.71      | 4.76       |

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
Table S8: Doublet excitation energy (in eV) of atom Na. Experimental data were obtained from Ref S41

| AO | Exp | LDA | BLYP | B3LYP | LOSC-LDA | LOSC-BLYP | LOSC-B3LYP |
|----|-----|-----|------|-------|----------|-----------|------------|
| 3p | 2.10| 2.86| 3.04 | 2.86  | 2.48     | 2.70      | 2.60       |
| 4s | 3.19| 4.52| 5.34 | 4.83  | 3.29     | 4.04      | 3.82       |
| 3d | 3.62| 5.10| 5.81 | 5.33  | 3.93     | 4.66      | 4.38       |
| 4p | 3.75| 5.15| 5.89 | 5.39  | 3.81     | 4.49      | 4.28       |
| 5s | 4.12| 5.64| 6.37 | 5.87  | 3.90     | 4.63      | 4.48       |
| 4d | 4.28| 5.85| 6.53 | 6.04  | 4.14     | 4.93      | 4.73       |
| 5p | 4.34| 5.88| 6.62 | 6.11  | 4.08     | 4.80      | 4.66       |
| 6s | 4.51| 6.10| 6.82 | 6.32  | 4.15     | 4.89      | 4.77       |
| 6p | 4.62| 6.21| 6.95 | 6.44  | 4.24     | 4.95      | 4.85       |
| 5d | 4.59| 6.34| 7.00 | 6.52  | 4.60     | 5.29      | 5.16       |
| 7s | 4.71| 6.41| 7.06 | 6.56  | 4.34     | 4.97      | 4.92       |
| 7p | 4.78| 6.78| 7.13 | 6.63  | 4.35     | 5.08      | 4.99       |

MAE 1.52 2.16 1.69 0.25 0.57 0.42
MSE 1.52 -1.15 1.85 0.07 -0.29 -0.06

Table S9: Singlet excitation energy (in eV) of atom Be. Experimental data were obtained from Ref S41

| AO | Exp | LDA | BLYP | B3LYP | LOSC-LDA | LOSC-BLYP | LOSC-B3LYP |
|----|-----|-----|------|-------|----------|-----------|------------|
| 2p | 5.28| 5.68| 2.49 | 5.60  | 5.56     | 4.70      | 5.59       |
| 3s | 6.78| 9.02| 6.14 | 8.98  | 7.27     | 7.54      | 7.42       |
| 3p | 7.46| 9.77| 6.66 | 9.54  | 7.90     | 7.86      | 7.88       |
| 3d | 7.99| 10.29| 7.30| 10.08 | 8.44     | 8.32      | 8.34       |
| 4s | 8.09| 10.67| 6.91| 9.96  | 8.17     | 7.50      | 7.86       |
| 4p | 8.31| 10.90| 7.11| 10.19 | 8.37     | 7.79      | 8.14       |
| 4d | 8.53| 11.08| 7.37| 10.40 | 8.41     | 8.07      | 8.32       |
| 5s | 8.59| 11.25| 7.48| 10.53 | 8.44     | 7.91      | 8.22       |
| 5p | 8.69| 11.35| 7.56| 10.61 | 8.55     | 7.97      | 8.29       |
| 5d | 8.80| 11.55| 7.87| 10.87 | 8.84     | 8.47      | 8.27       |
| 6s | 8.84| 11.52| 7.78| 10.84 | 8.55     | 8.63      | 8.86       |
| 6p | 8.90| 11.57| 7.82| 10.88 | 8.57     | 8.04      | 8.41       |

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
Table S10: Triplet excitation energy (in eV) of atom Be. Experimental data were obtained from Ref S41

| AO | Exp | LDA | BLYP | B3LYP | LOSC-LDA | LOSC-BLYP | LOSC-B3LYP |
|----|-----|-----|------|-------|----------|-----------|------------|
| 2p | 2.72| 1.59| 1.38 | 5.04  | 1.86     | 1.54      | 1.88       |
| 3s | 6.46| 8.37| 7.87 | 7.74  | 6.90     | 6.22      | 6.45       |
| 3p | 7.30| 9.24| 8.73 | 8.63  | 7.70     | 7.01      | 7.26       |
| 3d | 7.69| 9.62| 9.21 | 9.10  | 8.18     | 7.55      | 7.77       |
| 4s | 8.00| 10.52|10.05|9.83  |8.08      |7.49      |7.80       |
| 4p | 8.28| 10.77|10.32|10.07 |8.29      |7.69      |7.97       |
| 4d | 8.42| 10.92|10.48|10.23 |8.43      |7.86      |8.12       |
| 5s | 8.56| 11.19|10.73|10.47 |8.39      |7.81      |8.21       |
| 5p | 8.69| 11.29|10.85|10.59 |8.48      |7.94      |8.31       |
| 5d | 8.75| 11.42|10.97|10.74 |8.71      |8.14      |8.55       |
| 6s | 8.82| 11.49|11.06|10.78 |8.53      |8.02      |8.41       |
| 6p | 8.89| 11.54|11.15|10.86 |8.54      |8.07      |8.45       |
| 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     |            |

Table S11: Singlet excitation energy (in eV) of atom Mg. Experimental data were obtained from Ref S41

| AO | Exp | LDA | BLYP | B3LYP | LOSC-LDA | LOSC-BLYP | LOSC-B3LYP |
|----|-----|-----|------|-------|----------|-----------|------------|
| 3p | 4.35| 5.00| 5.61 | 5.13  | 4.62     | 5.28      | 4.86       |
| 4s | 5.39| 7.48| 6.80 | 6.52  | 6.26     | 5.44      | 5.51       |
| 3d | 5.75| 8.33| 8.21 | 7.63  | 7.02     | 6.79      | 6.48       |
| 4p | 6.12| 8.37| 7.75 | 7.48  | 6.94     | 6.22      | 6.26       |
| 5s | 6.52| 9.00| 8.52 | 8.19  | 6.96     | 6.41      | 6.57       |
| 4d | 6.59| 9.26| 8.96 | 8.55  | 7.29     | 6.74      | 6.94       |
| 5p | 6.78| 9.29| 8.83 | 8.50  | 7.25     | 6.70      | 6.89       |
| 6s | 6.97| 9.55| 9.21 | 8.84  | 7.27     | 6.90      | 7.03       |
| 5d | 6.98| 9.70| 9.48 | 9.06  | 7.36     | 7.25      | 7.13       |
| 6p | 7.09| 9.72| 9.39 | 9.02  | 7.75     | 7.07      | 7.38       |
| 7s | 7.19| 9.81| 9.53 | 9.13  | 7.40     | 7.05      | 7.21       |
| 7p | 7.26| 9.88| 9.59 | 9.20  | 7.44     | 7.06      | 7.27       |
| 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      |            |
Table S12: Triplet excitation energy (in eV) of atom Mg. Experimental data were obtained from Ref S41

| AO | Exp | LDA | BLYP | B3LYP | LOSC-LDA | LOSC-BLYP | LOSC-B3LYP |
|----|-----|-----|------|-------|----------|-----------|------------|
| 3p | 2.71| 2.64| 2.57 | 2.61  | 2.36     | 2.19      | 2.36       |
| 4s | 5.11| 7.03| 6.67 | 6.45  | 5.69     | 5.21      | 5.39       |
| 3d | 5.95| 7.22| 7.03 | 6.93  | 6.07     | 5.63      | 5.88       |
| 4p | 5.93| 8.05| 7.62 | 7.37  | 6.66     | 6.09      | 6.22       |
| 5s | 6.43| 8.90| 8.47 | 8.15  | 6.96     | 6.37      | 6.53       |
| 4d | 6.72| 9.08| 8.65 | 8.35  | 7.23     | 6.65      | 6.79       |
| 5p | 6.73| 9.20| 8.78 | 8.46  | 7.16     | 6.65      | 6.82       |
| 6s | 6.93| 9.50| 9.17 | 8.81  | 7.29     | 6.87      | 7.03       |
| 5d | 7.06| 9.62| 9.26 | 8.92  | 7.47     | 7.04      | 7.21       |
| 6p | 7.07| 9.64| 9.35 | 8.98  | 7.42     | 6.99      | 7.16       |
| 7s | 7.17| 9.79| 9.50 | 9.11  | 7.41     | 7.04      | 7.21       |
| 7p | 7.25| 9.86| 9.57 | 9.19  | 7.44     | 7.04      | 7.23       |
| 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      |            |
## Supplementary polyacene geometry

### Benzene

|  |  |  |  |
|---|---|---|---|
| C | 0.0000 | 1.3966 | 0.0000 |
| C | 1.2095 | 0.6983 | 0.0000 |
| C | 1.2095 | -0.6983 | 0.0000 |
| C | 0.0000 | -1.3966 | 0.0000 |
| C | -1.2095 | -0.6983 | 0.0000 |
| C | -1.2095 | 0.6983 | 0.0000 |
| H | 0.0000 | 2.4836 | 0.0000 |
| H | 2.1509 | 1.2418 | 0.0000 |
| H | 2.1509 | -1.2418 | 0.0000 |
| H | 0.0000 | -2.4836 | 0.0000 |
| H | -2.1509 | -1.2418 | 0.0000 |
| H | -2.1509 | 1.2418 | 0.0000 |

### Naphthalene

|  |  |  |  |
|---|---|---|---|
| C | 0.0 | 0.714951 | 0.0 |
| C | 0.0 | -0.714951 | 0.0 |
| C | 2.426869 | 0.706561 | 0.0 |
| C | -2.426869 | 0.706561 | 0.0 |
| C | 2.426869 | -0.706561 | 0.0 |
| C | -2.426869 | -0.706561 | 0.0 |
| C | 1.242318 | 1.398661 | 0.0 |
| C | -1.242318 | 1.398661 | 0.0 |
| C | 1.242318 | -1.398661 | 0.0 |

S41
|   | X       | Y       | Z       |
|---|---------|---------|---------|
| C | -1.2423 | -1.3986 | 0.0     |
| H | 3.3690  | 1.2416  | 0.0     |
| H | -3.3690 | 1.2416  | 0.0     |
| H | 3.3690  | -1.2416 | 0.0     |
| H | -3.3690 | -1.2416 | 0.0     |
| H | 1.2414  | 2.4831  | 0.0     |
| H | -1.2414 | 2.4831  | 0.0     |
| H | 1.2414  | -2.4831 | 0.0     |
| H | -1.2414 | -2.4831 | 0.0     |
| C | 0.0     | 1.2204  | 0.7208  |
| C | 0.0     | -1.2204 | 0.7208  |
| C | 0.0     | 1.2204  | -0.7208 |
| C | 0.0     | -1.2204 | -0.7208 |
| C | 0.0     | 1.4000  | 1.4003  |
| C | 0.0     | -1.4000 | -1.4003 |
| C | 0.0     | 2.4740  | 1.4031  |
| C | 0.0     | -2.4740 | 1.4031  |
| C | 0.0     | 2.4740  | -1.4031 |
| C | 0.0     | -2.4740 | -1.4031 |
| C | 0.0     | 3.6508  | 0.7114  |
| C | 0.0     | -3.6508 | 0.7114  |
| C | 0.0     | 3.6508  | -0.7114 |
| C | 0.0     | -3.6508 | -0.7114 |
| H | 0.0     | 0.0     | 2.4853  |

**Anthracene**

|   | X       | Y       | Z       |
|---|---------|---------|---------|
| C | 0.0     | 1.2204  | 0.7208  |
| C | 0.0     | -1.2204 | 0.7208  |
| C | 0.0     | 1.2204  | -0.7208 |
| C | 0.0     | -1.2204 | -0.7208 |
| C | 0.0     | 1.4000  | 1.4003  |
| C | 0.0     | -1.4000 | -1.4003 |
| C | 0.0     | 2.4740  | 1.4031  |
| C | 0.0     | -2.4740 | 1.4031  |
| C | 0.0     | 2.4740  | -1.4031 |
| C | 0.0     | -2.4740 | -1.4031 |
| C | 0.0     | 3.6508  | 0.7114  |
| C | 0.0     | -3.6508 | 0.7114  |
| C | 0.0     | 3.6508  | -0.7114 |
| C | 0.0     | -3.6508 | -0.7114 |
| H | 0.0     | 0.0     | 2.4853  |
Tetracene

30

C 0.0 0.724345 0.0
C 0.0 -0.724345 0.0
C 1.232442 1.402849 0.0
C -1.232442 1.402849 0.0
C 1.232442 -1.402849 0.0
C -1.232442 -1.402849 0.0
C 2.443772 0.724216 0.0
C -2.443772 0.724216 0.0
C 2.443772 -0.724216 0.0
C -2.443772 -0.724216 0.0
C 3.702747 1.405473 0.0
C -3.702747 1.405473 0.0
C 3.702747 -1.405473 0.0
C -3.702747 -1.405473 0.0
C 4.875977 0.713742 0.0
Pentacene

36

C  0.0  1.223172  0.726794
C  0.0  -1.223172  0.726794
C  0.0  1.223172  -0.726794
C  0.0  -1.223172  -0.726794
C  0.0  3.668639  0.726066
C  0.0  -3.668639  0.726066
C  0.0  3.668639  -0.726066
C  0.0  -3.668639  -0.726066
C  0.0  2.461665  1.404459
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | 0.728760     | 0.0          | 0.0          |
| C       | -0.728760    | 0.0          | 0.0          |
| C       | 1.406190     | 1.229341     | 0.0          |
| C       | -1.406190    | 1.229341     | 0.0          |
| C       | 1.406190     | -1.229341    | 0.0          |
| C       | -1.406190    | -1.229341    | 0.0          |
| C       | 0.728192     | 2.447851     | 0.0          |
| C       | -0.728192    | 2.447851     | 0.0          |
| C       | 0.728192     | -2.447851    | 0.0          |
| C       | -0.728192    | -2.447851    | 0.0          |
| C       | 1.405376     | 3.689513     | 0.0          |
| C       | -1.405376    | 3.689513     | 0.0          |
| C       | 1.405376     | -3.689513    | 0.0          |
| C       | -1.405376    | -3.689513    | 0.0          |
| C       | 0.727090     | 4.894222     | 0.0          |
| C       | -0.727090    | 4.894222     | 0.0          |
| C       | 0.727090     | -4.894222    | 0.0          |
| C       | -0.727090    | -4.894222    | 0.0          |
| C       | 1.407386     | 6.157229     | 0.0          |
| C       | -1.407386    | 6.157229     | 0.0          |
| C       | 1.407386     | -6.157229    | 0.0          |
| C       | -1.407386    | -6.157229    | 0.0          |
| C       | 0.715651     | 7.327785     | 0.0          |
| C       | -0.715651    | 7.327785     | 0.0          |
| C       | 0.715651     | -7.327785    | 0.0          |
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