

Predicting fundamental gaps accurately from density functional theory with non-empirical local range separation

Cite as: *J. Chem. Phys.* **160**, 181101 (2024); doi: [10.1063/5.0204379](https://doi.org/10.1063/5.0204379)

Submitted: 21 February 2024 • Accepted: 22 April 2024 •

Published Online: 8 May 2024



View Online



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Moritz Brütting,¹ Hilke Bahmann,² and Stephan Kümmel^{1,a)}

AFFILIATIONS

¹Theoretical Physics IV, University of Bayreuth, 95440 Bayreuth, Germany

²Physical and Theoretical Chemistry, University of Wuppertal, 42097 Wuppertal, Germany

^{a)}Author to whom correspondence should be addressed: stephan.kuemmel@uni-bayreuth.de

ABSTRACT

We present an exchange–correlation approximation in which the Coulomb interaction is split into long- and short-range components and the range separation is determined by a non-empirical density functional. The functional respects important constraints, such as the homogeneous and slowly varying density limits, leads to the correct long-range potential, and eliminates one-electron self-interaction. Our approach is designed for spectroscopic purposes and closely approximates the piecewise linearity of the energy as a function of the particle number. The functional’s accuracy for predicting the fundamental gap in generalized Kohn–Sham theory is demonstrated for a large number of systems, including organic semiconductors with a notoriously difficult electronic structure.

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I. INTRODUCTION

Density functional theory (DFT)^{1–3} is a central pillar of electronic structure theory as it typically offers useful accuracy at a moderate computational cost. The first and traditional purpose for which DFT is employed is the prediction of the ground-state energy and structural properties that follow from it. However, DFT is also used for the second purpose of calculating spectroscopic properties. One of the most important spectroscopic observables is the fundamental gap, defined by the difference between the first ionization potential (IP) and the first electron affinity (EA),

$$\Delta_g = \text{IP} - \text{EA}. \quad (1)$$

The gap determines the character of a material, e.g., as a metal or semiconductor, and in today’s research, predicting Δ_g reliably and efficiently⁴ is of particular relevance because of the quest for energy-converting materials: Δ_g is a decisive factor for determining whether a material is suitable for, e.g., a solar cell or a photo-catalyst.^{5,6}

The predictive power of a DFT calculation hinges on the accuracy of the employed exchange–correlation (xc) approximation. For DFT’s first purpose, i.e., predicting the ground-state energy, years

of development have equipped the community with an impressive selection of xc approximations, which allow one to target the level of accuracy and computational cost that is required for the task at hand, e.g., see Refs. 1, 2, 7, and 8 for reviews. In fact, for predicting the ground-state energy, by now DFT can rival wavefunction-based methods.⁹

For the second purpose, i.e., predicting spectroscopic observables and especially Δ_g , the situation is more complex. This is to a certain extent a natural consequence of the very nature of DFT: it focuses on the density, and orbitals were originally introduced just as auxiliary objects for evaluating the kinetic energy. Thus, it is no surprise that the single particle gap between the lowest unoccupied (L) and highest occupied (H) orbital,

$$\Delta_\epsilon = \epsilon_L - \epsilon_H \quad (2)$$

in Kohn–Sham theory does not correspond to Δ_g even for the exact xc functional.^{10–13} In a quasi-particle picture, the physical processes corresponding to IP and EA, i.e., inserting or removing an electron, can be considered as creating a quasi-electron or quasi-hole, respectively. These quasi-particles contain the response effects of the

correlated many-electron system to the presence of the extra electron or hole. In many-body perturbation theory, the GW approach^{14–16} provides for a natural way of calculating the quasi-particle energies.

By going from Kohn–Sham to generalized Kohn–Sham theory, it is possible to establish the equality $\Delta_g = \Delta_e$ within DFT.¹⁷ While one can define more than one non-interacting reference systems in generalized Kohn–Sham theory, generalized Kohn–Sham is not a heuristic construct¹⁸ and the gap is a well-defined observable.^{19,20} Thus, being able to predict the many-body observable Δ_g reliably in an inexpensive single particle-like calculation is extremely attractive. However, constructing xc approximations that fulfill this promise in practice is a challenge because several of DFT's most demanding aspects have to be addressed for reliable gap prediction: one-electron self-interaction must be corrected to avoid erroneous offsets of the occupied eigenvalues,²¹ a non-zero derivative discontinuity is required in the Kohn–Sham scheme to correctly lift up the unoccupied eigenvalues,^{11–13,22} the xc potential must have the proper asymptotics,^{23,24} the energy should be a straight line as a function of particle number between integers,^{10,25,26} and correspondingly, the highest occupied eigenvalue should not depend on its occupation number.^{27–29}

II. RANGE SEPARATION

A decisive step forward in the reliability of DFT predicted gaps was reached based on range separation, i.e., by splitting the Coulomb interaction into a long- and a short-range component.^{30–32} In practice, this is often done in the form

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \underbrace{\frac{\text{erf}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}}_{\text{long range}} + \underbrace{\frac{1 - \text{erf}(\omega|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}}_{\text{short range}}, \quad (3)$$

where the range-separation parameter, ω , plays a decisive role. In recent years, range-separated hybrid (RSH) functionals have mostly been developed along two lines.

In one line of development, successful functionals have been constructed empirically by determining a value for ω by fitting to reference data.^{8,33–38} Many different forms have been devised, e.g., using exact exchange in either short- or long-range or both, and possibly combining Eq. (3) with further concepts, such as the one of local hybrids.^{39–42} In this class of functionals, there are two recently developed ones that are particularly interesting in the present context because they lead to promising results for both binding effects and spectroscopic properties. The DM21⁴³ functional reaches remarkable accuracy; however, it is hard to deduce insight into xc effects from the underlying trained neural network. The ω LH22t^{44–46} functional is of a different nature. Its form is guided by functional development concepts, with nine parameters that are fitted empirically, and it is accurate for many ground- and excited-state observables. As it is one of the most accurate functionals with an exceptionally wide range of application, we return to ω LH22t below for comparison.

A second, alternative way of using Eq. (3) is the concept of determining ω by optimal tuning (OT).^{47–49} Here, we refer to OT that uses exact exchange in the long range with just one parameter ω that is determined non-empirically: It exploits the

IP theorem^{10,28} and adjusts ω such that the frontier eigenvalues become as close as possible to IP and EA as calculated from total energy differences between the neutral, the cation, and the anion systems. The OT approach is specifically designed to yield a functional for spectroscopy. It has been extremely successful and, thus inspired RSHs have been further developed, e.g., to incorporate the effects of screening.^{50–53} OT allows avoiding the empirical fitting of parameters. This is desirable as the final form of empirical approaches depends on the details of the fitting procedure,⁵⁴ and developing non-empirical functionals is part of the quest for deeper understanding and universality in DFT.^{3,55,56}

The widespread use of OT underlines the strong need for functionals that predict spectroscopic properties reliably. However, OT also has non-negligible drawbacks. First, the tuning is computationally involved, requiring many calculations also for charged systems. Second, tuning violates size consistency,^{47,57,58} and the system-specific determination of ω can have further surprising consequences.⁵⁹ Third, the applicability of OT is limited by intrinsic questions of consistency. Tuning can fail, e.g., for donor–acceptor systems of largely different chemical nature. More importantly, yet, for systems with delocalized electrons, the tuning procedure spuriously yields ever smaller values of ω for systems of increasing size.^{60,61} Thus, the functional becomes increasingly semilocal, and consequently, the well-known problems of semilocal functionals, such as too low fundamental gaps,⁶² reappear. Ultimately, these failures have their origin in the fact that OT is system-specific, and thus, ω is turned into a density functional, but one that is only very implicitly defined. One can mitigate the problems by judiciously tuning only for a subsystem.^{63–66} However, this works reliably only up to a certain system size, and the originally high predictive power of OT might eventually be compromised.

III. A CONSTRAINT-GUIDED EXCHANGE–CORRELATION FUNCTIONAL WITH LOCAL RANGE SEPARATION

These problems can be overcome by going from global to local range separation, i.e., one continues to use Eq. (3), yet makes ω an explicit density functional $\omega([n], \mathbf{r})$. In the following, we thus solve the problems that arise with the only implicitly defined density functional of OT, as the explicit dependence on the density naturally leads to different forms of $\omega([n], \mathbf{r})$ for different systems. At the same time, we avoid empiricism by designing $\omega([n], \mathbf{r})$ such that it fulfills the important fundamental constraints of the homogeneous electron gas, of the slowly varying density limit, and of being free from one-electron self-interaction.

Previous studies using local range separation^{67–71} focused on finding functionals for traditional ground-state properties and relied on empirically fitted parameters. Our aim here is different, as our focus is on constructing a functional that will allow reliably predicting the fundamental gap Δ_g from first principles. Therefore in our functional construction, we deliberately focus on those properties of the xc functional that are relevant for gap prediction, and not on atomization energies.

Making use of Eq. (3), one can write the xc energy in the form

$$E_{xc}^{\text{IRSH}} = E_x^{\text{LR,ex}} + E_x^{\text{SR,sl}} + E_c^{\text{sl}}. \quad (4)$$

Here, $E_x^{\text{LR,ex}}$ denotes exact long-range exchange, i.e., the Fock-integral evaluated with the first term on the right-hand side of Eq. (3). This choice by construction guarantees the correct long-range asymptotics of the potential. Here, $E_x^{\text{SR,sl}}$ and E_c^{sl} are semilocal functionals, taking into account short-range exchange and correlation, respectively. The key idea for the non-empirical construction is to use Eq. (4) in combination with the range-separation functional

$$\omega_\sigma(\mathbf{r}) = C_{\text{GE}} \frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})} \frac{1}{1 - \frac{1}{2}(z_\sigma(\mathbf{r})\zeta^2(\mathbf{r}) + z_\sigma(\mathbf{r}))}. \quad (5)$$

Here, $n_\sigma(\mathbf{r})$ is the spin-density, $|\nabla n_\sigma(\mathbf{r})|$ is its gradient, and $\tau_\sigma(\mathbf{r}) = \frac{1}{2} \sum_i |\nabla \phi_{i\sigma}(\mathbf{r})|^2$ is the non-interacting kinetic energy density (in Hartree atomic units). The functions $z_\sigma(\mathbf{r})$ and $\zeta^2(\mathbf{r})$ refer to the ratio of τ_σ and its single orbital (von Weizsäcker) limit, i.e., $z_\sigma = |\nabla n_\sigma|^2 / (8n_\sigma\tau_\sigma)$, and the spin-polarization, $\zeta = (n_\uparrow - n_\downarrow) / (n_\uparrow + n_\downarrow)$. $C_{\text{GE}} = \sqrt{5}/18 \approx 0.124226$ is a non-empirical coefficient (see below). We base the ω -dependent short-range exchange $E_x^{\text{sl,SR}}$ on the local density approximation (LDA) in the analytical form given in Ref. 72. The correlation

$$E_c^{\text{sl}} = \int d\mathbf{r} \left(\varepsilon_c^{\text{LDA}}[n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})] - \sum_\sigma z_\sigma(\mathbf{r}) \varepsilon_c^{\text{LDA}}[n_\sigma(\mathbf{r}), 0] \right) \quad (6)$$

is based on LDA with a self-interaction correction (SIC), where $\varepsilon_c^{\text{LDA}}$ is the correlation energy density in the parametrization by Perdew and Wang.⁷³

This functional is motivated by the following considerations. First, it respects the homogeneous-electron-gas limit: $\omega_\sigma(\mathbf{r})$ vanishes in this limit⁷¹ and the correlation energy of Eq. (6) reduces to LDA. Second, we incorporate the slowly varying limit (gradient expansion to second order) of the exchange energy density,⁷⁴

$\varepsilon_{x\sigma} = C_0 n_\sigma^{4/3} \left(1 + C_2 (|\nabla n_\sigma| / n_\sigma^{4/3})^2 + \dots \right)$, with $C_0 = -3(6\pi^2)^{1/3} / 4\pi$ and $C_2 = 10 / (81 \cdot 4(6\pi^2)^{2/3})$. This is ensured as our $\omega_\sigma(\mathbf{r})$ has

$$\omega_\sigma^{\text{GE}}(\mathbf{r}) = C_{\text{GE}} \frac{|\nabla n_\sigma(\mathbf{r})|}{n_\sigma(\mathbf{r})} \quad (7)$$

as the leading term of is gradient expansion, and the choice $C_{\text{GE}} = \sqrt{5}/18$ yields the proper gradient expansion coefficient.^{70,71}

Third, it corrects for one-electron self-interaction. Here, a delicate balance is required. If one corrects straightforwardly for one-electron self-interaction as done in Hartree–Fock or Perdew–Zunger SIC, one typically overcorrects. A manifestation of overcorrection is that the energy as a function of particle number, $E(N)$, is concave. On the other hand, if one does not correct enough, then the functional retains too much of its semilocal character, which manifests in a convex $E(N)$. However, a straight-line $E(N)$ is important for obtaining physically meaningful eigenvalues,^{26,75,76} and the straight-line condition provides a guide rail in functional construction in addition to the exact constraints. We can reach the proper balance with local range separation by using iso-orbital indicators and spin functions^{77–84} as done in Eq. (5) with the last multiplicative term on the right-hand side. This term tends to infinity when the denominator vanishes, making the functional go to full exact exchange in this case.^{68,71} How this limit is reached is controlled by z_σ and ζ . Here, z_σ distinguishes between the homogeneous-electron-gas limit ($z_\sigma \rightarrow 0$) and the *one-orbital* limit ($z_\sigma \rightarrow 1$). On the other hand, $z_\sigma \zeta^2$ is bound between its value in closed-shell systems or the homogeneous electron gas ($z_\sigma \zeta^2 \rightarrow 0$) and its value in *one-electron* regions ($z_\sigma \zeta^2 \rightarrow 1$). The linear combination of z_σ and $z_\sigma \zeta^2$ ensures that one-electron systems are fully self-interaction corrected, while other systems are subjected to a more moderate correction, with the spatial profile of the density being taken into account via the n_σ , ∇n_σ , and τ_σ contributions. The interplay between the homogeneous electron gas limit on the one hand and, on the other hand, ensuring a vanishing interaction for one-electron system while also guaranteeing

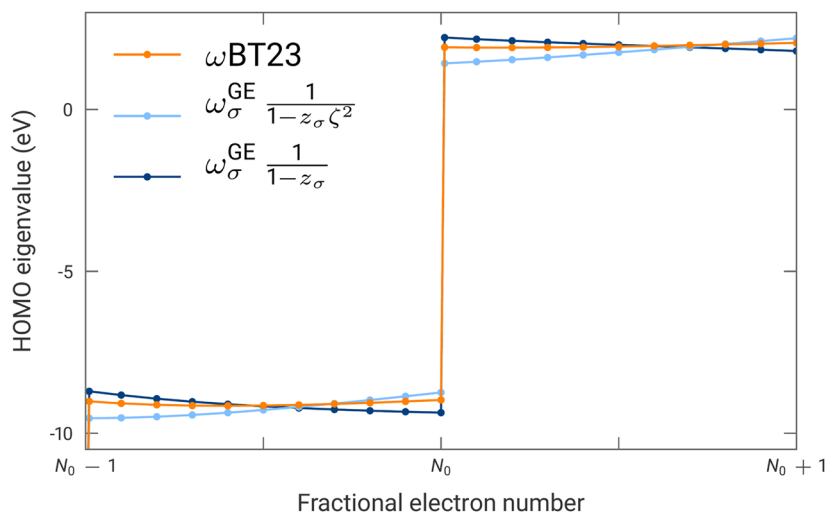


FIG. 1. Highest occupied eigenvalue of benzene as a function of the fractional electron number (N_0 electrons: neutral system) calculated with the functional of Eqs. (4)–(6), labeled ωBT23 . See the main text for a discussion of the other two curves.

a general correction, is also the guiding principle in the correlation functional of Eq. (6).^{85,114}

IV. RESULTS

Figure 1 shows the fractional charge behavior that our functional reaches for the paradigm case of the benzene molecule. It shows the dependence of ε_H on the particle number. This dependence directly reflects the curvature in $E(N)$.^{26–28,76,86} For our functional (labeled ω BT23, where the acronym “BT” refers to “Bayreuth,” the university city of the first author), the eigenvalue is independent of the particle number in an excellent approximation both below and above the integer. As a reference and to illustrate the above-mentioned balance, we also show the curves that would be obtained when one would only use either $1 - z_\sigma \zeta^2$ or $1 - z_\sigma$ in the denominator of the last term in Eq. (5). One would clearly obtain a positive or negative curvature in $E(N)$, respectively. That the linear combination of the two terms tends to balance their individual trends is an observation that we made for all systems for which we made this analysis.

These and all the following calculations involving local range separation were performed with a development version of TURBOMOLE,⁸⁷ into which we implemented our functional. The

self-consistent evaluation relies on the developments of Klawohn and Bahmann.⁶⁹ See the supplementary material for more details.

Having explained and verified the guiding principles of our functional construction, we proceed to use it for the prediction of fundamental gaps of a set of molecules.⁸⁸ We chose this set because it is ideally suited for several reasons: First, the molecules are practically relevant as they are typical for the type of systems that are used in organic electronics. Second, they cover a considerable range of sizes and chemical compositions. Third and most importantly, reliable reference data are available for this set: On the one hand, highly accurate results have been obtained in wavefunction-based calculations,⁸⁸ and on the other hand, several different versions of DFT⁸⁹ and diligently conducted GW calculations⁹⁰ have been reported for these systems. Figure 2 shows the fundamental gap calculated as the difference between the generalized Kohn–Sham frontier eigenvalues of our functional plotted against the wavefunction reference. One sees that there are a few systems for which the difference is as large as a few 0.1 eV, but overall, the results are close to the diagonal dashed line that indicates perfect agreement. The mean absolute error (MAE) across the set is 0.20 eV for ω BT23. This finding is put into perspective when one compares it to the accuracy reached with other methods. On the one hand, for the same set of molecules, OT with an individual adjustment of the range-separation parameter for each molecule leads to an MAE of

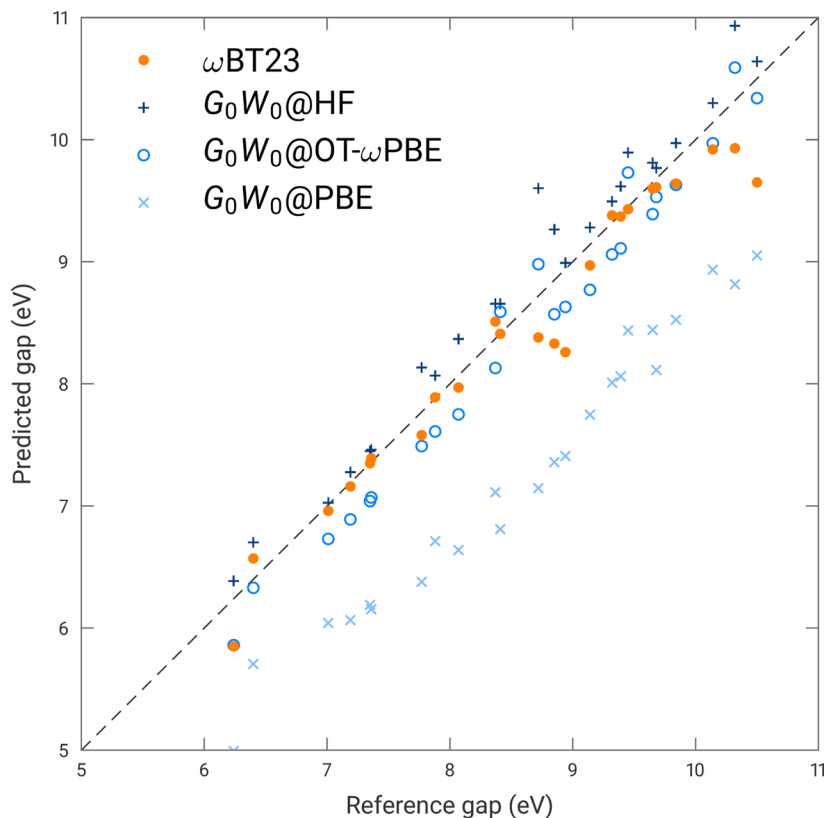


FIG. 2. Fundamental gaps of organic molecules calculated as the difference of the frontier eigenvalues of the ω BT23 density functional plotted against the reference gaps calculated from CCSD(T)⁸⁸ (cf. the supplementary material for raw data). Three variants of G_0W_0 ,^{89,90} namely, using PBE, Hartree–Fock, and OT- ω PBE as a starting point, respectively, are also shown. Ideal agreement is indicated by the dashed line.

0.38 eV.⁸⁹ On the other hand, Fig. 2 shows the gaps that are obtained with different variants of G_0W_0 : with a Perdew–Burke–Ernzerhof (PBE) calculation as the starting point, one finds a serious underestimation, whereas with Hartree–Fock (HF) as the starting point, one finds a slight overestimation. Putting G_0W_0 on top of OT- ω PBE, which has been identified⁹⁰ as one of the best possible GW approaches for this benchmark set, leads to an MAE of 0.26 eV.⁸⁹ Thus, gap prediction based on non-empirical generalized Kohn–Sham DFT with ω BT23 can clearly compete with both non-empirical OT and G_0W_0 with a diligently chosen starting point. While reaching this accuracy in the GW approach requires one to perform a DFT calculation with a range-separated hybrid first and then in addition the computationally expensive G_0W_0 calculation, our locally RSH functional yields the same accuracy from the DFT calculation alone. The fact that DFT can rival GW in accuracy has recently also been demonstrated for the ω LH22t functional, for which an MAE of 0.23 eV has been reported in Ref. 45 for the gaps of this set. In the supplementary material, we report further comparisons to ω LH22t.

The accuracy of our functional is also confirmed when looking at the eigenvalues of the organic semiconductor molecules NTCDA (i.e., 1,4,5,8-naphthalene-tetracarboxylic dianhydride) and PTCDA (i.e., 3,4,9,10-perylene-tetracarboxylic acid dianhydride), which have been studied in detail both experimentally and

theoretically, e.g., in Refs. 91–93. They constitute a formidable challenge to conventional DFT because of their mixture of delocalized and localized orbitals⁹⁴ and are also tricky for non-empirical optimal tuning⁹⁵ because a judiciously chosen fraction of short-range exact exchange is needed for a correct description.⁹⁶ For NTCDA, the first IP is 9.67 eV experimentally and 9.62 eV with ω BT23, and for PTCDA, the values are 8.20 and 8.16 eV, respectively. With a consistently chosen starting point, G_0W_0 yields 9.65 and 8.13 eV for the first IP.^{45,97} For the second IP, G_0W_0 yields 10.34 and 9.76 eV, respectively, whereas the numbers are 10.39 and 10.00 eV, respectively, with ω BT23. Thus, even for these particularly difficult systems, the ω BT23 results are in a similar trust range as the G_0W_0 results.

Finally, we check whether the non-empirical local range separation can remedy the issues that one encounters with optimal tuning for conjugated systems of increasing size. Figure 3 shows the fundamental gaps calculated with ω BT23 and OT- ω PBE⁶⁰ for the paradigm case of oligoacenes of increasing size, plotted as a function of the accurate wavefunction-based reference gaps.^{98,99} While the absolute accuracy achieved with optimal tuning is quite good for the smaller systems, the trend that the errors increase noticeably with the system size is clearly visible in the deviation from the diagonal dashed line. However, in particular larger-size systems with lower gaps are of technological interest. Therefore, it is reassuring to

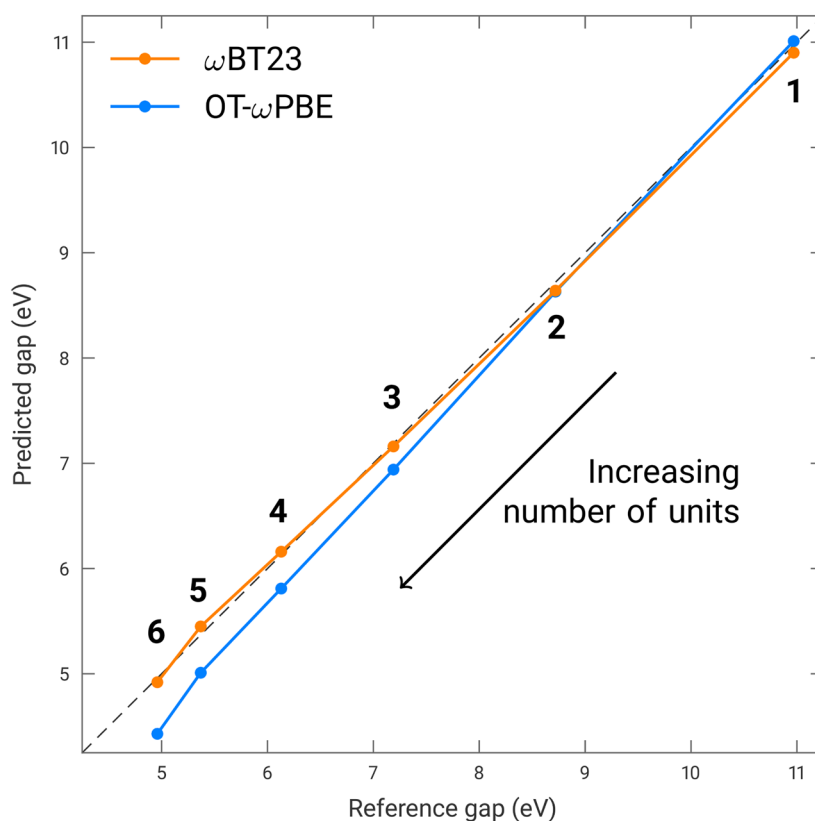


FIG. 3. Size dependence of the fundamental gap for the series of oligoacenes (from benzene to hexacene, i.e., one to six molecular units) calculated with the ω BT23 functional and OT- ω PBE⁶⁰ and plotted with respect to the reference gaps calculated from CCSD(T)^{98,99} (cf. the supplementary material for raw data).

see that with our local range separation the accuracy is consistently high (deviations below 0.1 eV) for all system sizes, with an MAE of 0.06 eV.

V. CONCLUSION AND OUTLOOK

On summarizing our findings, we conclude that the successful concept of RSHs becomes particularly powerful when the range separation is governed by a density functional. We have developed such an explicit functional from first principles for the purposes of predicting the fundamental gap without adjustable parameters. Our construction is guided by the constraints of yielding the proper long-range asymptotic potential, respecting the homogeneous electron gas limit, fulfilling the second-order gradient expansion, and eliminating one-electron self-interaction. This leads to a functional for which the energy as a function of the particle number approximates a straight line, which can be interpreted as a sign for the reduction of many-electron self-interaction.^{100,101}

In view of this success, one should nevertheless be aware that ω BT23 is not a panacea. We report some atomization energies and barrier heights in the supplementary material. For ground-state energetics, other functionals, e.g., the ones from Refs. 44 and 71, are considerably more accurate. Furthermore, calculations with a constant range-separation parameter run efficiently in many codes. Therefore, we do not expect ω BT23 to generally replace OT or well-calibrated general-purpose functionals. However, ω BT23's specific non-empirical design for spectroscopic purposes makes it ideal for applications where other methods, such as OT or GW, reach their limits, i.e., its intended application is similar to the one of OT functionals.

In this context, having the density functional $\omega([n], \mathbf{r})$ instead of a (tuned) parameter has several advantages. First, it makes the functional universal. Thus eliminating the need for the system specific determination of parameters not only simplifies computational procedures but also avoids the size-consistency problem of OT. Second, whereas OT may fail for, e.g., donor-acceptor systems that require largely different values of the range-separation parameter for donor and acceptor, respectively, the functional $\omega([n], \mathbf{r})$ can adjust individually to the separate components. Third, possible problems that OT faces for systems of increasing size are avoided. As a final outlook, we note that local range separation is promising not only from the perspective of DFT but also from the one of time-dependent DFT (TDDFT). Based on general arguments¹⁰² and the experience from optimally tuned RSHs^{24,48,76,103–105} and range-separated local hybrids,^{44,45} one expects that functionals that yield frontier eigenvalues that reflect ionization potential and electron affinity, respectively, will also be accurate in TDDFT for charge-transfer excitations. Implementing the equations of TDDFT for RSHs with local range separation is beyond the scope of the present work. However, the concept of developing RSHs with an explicit density dependence, an example of which we have given in this paper, is also promising from this perspective.

SUPPLEMENTARY MATERIAL

The supplementary material, which includes Refs. 106–113, contains computational details, the data underlying Figs. 2 and 3,

further comparison of ω BT23 and ω LH22t, and information about atomization energies and barrier heights with ω BT23.

ACKNOWLEDGMENTS

S.K. acknowledges the financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) Project No. 457582427 and from the Bavarian State Ministry of Science, Research, and the Arts for the Collaborative Research Network “Solar Technologies go Hybrid.” M.B. and S.K. acknowledge the support from the Elite Study Program “Biological Physics” of the Elite Network of Bavaria. M.B. further acknowledges the support by the “Studienstiftung des Deutschen Volkes” and by the University of Bayreuth Graduate School. H.B. acknowledges funding from the DFG, Project No. 418140043.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

M.B. and S.K. conceptualized the work and discussed the functional construction. H.B. participated in the discussions about functional construction. M.B. implemented the functional, did the calculations, and prepared the figures in discussion with S.K. M.B. and S.K. wrote the manuscript, with comments and proofreading from H.B.

Moritz Brütting: Conceptualization (equal); Formal analysis (equal); Investigation (equal); Software (lead); Validation (lead); Visualization (lead); Writing – original draft (equal); Writing – review & editing (equal). **Hilke Bahmann:** Investigation (supporting); Software (supporting); Writing – review & editing (equal). **Stephan Kümmel:** Conceptualization (equal); Formal analysis (equal); Funding acquisition (lead); Investigation (equal); Project administration (lead); Supervision (lead); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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