Supporting Information for: Delocalization error and 'functional tuning' in Kohn-Sham calculations of molecular properties

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1. Definition of acronyms

2. Further details regarding the CT problem of time-dependent Kohn-Sham theory

3. Detailed description of the tuning procedure, additional data for para-nitroaniline

Acronyms used in the article

1DT – one-dimensional IP-tuning, γ -tuning **2DT** – two-dimensional IP-tuning, α - γ -tuning **acac** – acetylacetonate **B3LYP** – Becke 3-parameter Lee-Yang-Parr functional with $\alpha = 02$ B3LYP – Becke-Lee-Yang-Parr functional **BNL** – Baer-Neuhauser-Lifshifts functional with $\gamma = 0.33$ a.u., $\alpha = 0.0$, $\beta = 1.0$ **BP** – Becke-Perdew functional BTX-D – brevetoxin-D CAM - Coulomb-attenuated method CAM-B3LYP - Coulomb-attenuated method Becke 3-parameter Lee-Yang-Parr functional with $\gamma = 0.33$ a.u., $\alpha = 0.19$, $\beta = 0.46$ CC2 – second-order approximate coupled cluster singles and doubles model CC – coupled-cluster CD – circular dichroism **CIS(D)** – configuration interaction singles with perturbative treatment of doubles **CT** – charge transfer **DAN** – *N*,*N*-dimethyl-4-nitroaniline **DANS** – (*E*)-*N*,*N*-dimethyl-4-(4-nitrostyryl)aniline **DE** – delocalization error **EA** – electron affinity EFG – electric field gradient **EPR** – electron paramagnetic resonance **eX** – exact exchange GGA – generalized gradient approximation H, HOMO - highest occupied molecular orbital **HF** – Hartree-Fock, HF theory **hfc** – hyperfine coupling **IP** – ionization potential **KST** – Kohn-Sham theory L, LUMO – lowest unoccupied molecular orbital LC – long-range correction **LC-PBE0** – long-range corrected Perdew-Burke-Ernzerhof hybrid functional with $\gamma = 0.3$ a.u., $\alpha = 0.25, \beta = 0.75$ **LC-PBE0**^{*} – long-range corrected Perdew-Burke-Ernzerhof hybrid functional with $\alpha = 0.25$, $\beta = 0.75$ and system-specific IP-tuned γ

LC-PBEh^{*} – long-range corrected Perdew-Burke-Ernzerhof hybrid functional with system-specific IP-tuned γ and $\alpha = 1 - \beta$

LC-PBE – long-range corrected Perdew-Burke-Ernzerhof functional with $\gamma = 0.3$ a.u., $\alpha = 0.0$, $\beta = 1.0$

LC-PBE^{*} – long-range corrected Perdew-Burke-Ernzerhof functional with $\alpha = 0.0$, $\beta = 1.0$ and system-specific IP-tuned γ

- LDA local density approximation
- LMO localized molecular orbital

LP – lone pair

- MAE mean absolute deviation
- MM matrix model
- $MP2 M\emptyset$ ller-Plesset second-order perturbation method
- \mathbf{NBO} natural bond obital
- NLO non-linear optics
- NMR nuclear magnetic resonance
- NQCC nuclear quadrupole coupling constant
- **OR** optical rotation
- **PBE0** Perdew-Burke-Ernzerhof hybrid functional with $\alpha = 0.25$
- PBE Perdew-Burke-Ernzerhof functional
- **p-NA** *para*-nitroaniline
- **RSE** range-separation exchange
- S singlet
- SCE static correlation error
- \mathbf{SOS} sum over states
- \mathbf{T} triplet
- TD time dependent
- ${\bf TTP}-tetraphenyl porphyrin$
- **WFT** wavefunction theory
- \mathbf{XC} exchange-correlation

Response calculations with KST and TD-KST: The impact of approximations illustrated by the charge-transfer (CT) problem for excitation energies

When KST and TD-KST are applied to the calculation of atomic and molecular response properties, the use of approximate functionals reveals problems that are related to the breakdown of KST in other areas. One particularly well publicized and well understood problem is the treatment of charge-transfer (CT) excitations by TD-KST linear response theory.^{1–4} Consider a CT excitation from a donor (*D*) to an acceptor (*A*) moiety separated by a large distance *R*, with the system overall being neutral and possessing a singlet ground state. The CT excited state can be approximated by a pair of point charges, an electron and a hole, at the distance *R*. The CT excitation energy is then roughly (atomic units, a.u.)

$$E_{\rm CT} \approx {\rm IP}^D - {\rm EA}^A - 1/R \tag{S1}$$

Here, IP^{D} is the ionization potential of the donor and EA^{A} is the electron affinity of the acceptor. In the limit $R \to \infty$ the energy approaches $E_{CT} \approx IP^{D} - EA^{A}$, which is simply the energy it takes to remove the electron from the donor minus the energy gained from attaching it to the acceptor. The -1/R term is the electron-hole electrostatic interaction energy in a.u. A two-orbital (2-level) model derived from time-dependent HF (TD-HF) theory or from TD-KST for an occupied canonical orbital φ_i centered on the donor and an unoccupied φ_a centered on the acceptor, with orbitals energies ε_i , ε_a , gives⁵

$$E_{\rm CT} \approx \varepsilon_a - \varepsilon_i \begin{cases} +[ai|f_{\rm XC}|ia] & ({\rm TD-KST}) \\ -[ii|r_{12}^{-1}|aa] & ({\rm TD-HF}) \end{cases} + \begin{array}{c} 2[ai|r_{12}^{-1}|ia] \\ (\text{singlet excitation}) \end{cases}$$
(S2)

Here, the shorthand notation means $[ab|\hat{O}|cd] = \int \varphi_a^*(\mathbf{r}_1)\varphi_c^*(\mathbf{r}_2)\hat{O}(\mathbf{r}_1,\mathbf{r}_2)\varphi_b(\mathbf{r}_1)\varphi_d(\mathbf{r}_2)d^3r_1d^3r_2$. For the operator $\hat{O} = r_{12}^{-1}$ we have the usual electron-repulsion integrals. The operator f_{XC} is formally the frequency-dependent linear response XC kernel. Note that f_{XC} is not the same for singlet and triplet excitations if it is obtained from a functional that depends on the spin-density, but the two variants share a common component. With the adiabatic approximation and a semi-local XC potential, $f_{XC}(\mathbf{r}_1, \mathbf{r}_2, \omega) = f_{XC}(\mathbf{r}_1) \cdot \delta(\mathbf{r}_2 - \mathbf{r}_1)$ (also, $[ai|f_{XC}|ia] = [aa|f_{XC}|ii]$). The adiabatic approximation is used for the vast majority of TD-KST computations currently performed. The term $+2[ai|r_{12}^{-1}|ia]$ containing the exchange integral between orbitals φ_a, φ_i is common to TD-HF and TD-KST; it is absent for triplet excitations.⁶ It is important to keep in mind that the orbital energies and the orbital shapes are different in KST and HF. Further, it is emphasized that the common term $+2[ai|r_{12}^{-1}|ia]$ in Equation (S2) originates from the Coulomb ('Hartree') component of the potential, which is common to HF and KST except that it is calculated from different sets of orbitals. The $[ai|f_{XC}|ia]$ and $-[ii|r_{12}^{-1}|aa]$ terms in the TD-KST and TD-HF expressions, respectively, have their origin in the perturbation of the XC and HF-exchange component of the potential.

Suppose that the D/A orbitals in question are the highest occupied molecular orbital (HOMO, H) and the lowest unoccupied MO (LUMO, L). In HF theory, per Koopmans' theorem, the HOMO-LUMO gap (HLG), $\varepsilon_L - \varepsilon_H$, approximates IP^D-EA^A. For spatially separated orbitals, the exchange integral goes to zero much faster than 1/R and can be neglected. Further, for increasingly spatially separated orbitals $-[ii|r_{12}^{-1}|aa]$ is increasingly well approximated by -1/R. The HF expression for the two-level model then gives a reasonable approximation for Equation (S1), along with the correct -1/R asymptotic behavior at large R.

In a KST setup with a semi-local LDA or GGA XC potential, sometimes referred to as 'pure' KST, $[ai|f_{XC}|ia]$ vanishes exponentially for large *R* similarly to the exchange integral. The -1/R asymptotic behavior of the CT excitation energy is therefore not obtained. Furthermore, while in exact KST $-\epsilon_{\rm H} = IP$ exactly,^{7–9} LDA and GGA potentials typically afford $|\epsilon_i| < |IP|$, where the difference may easily reach several eV. At the same time, the LUMO approximates an excitation rather than an electron detachment,¹⁰ i.e. typically $|\epsilon_a| < |EA|$. As a result, not only does the TD-KST CT energy expression miss the asymptotic -1/R but the orbital energy gap is also typically much smaller than IP^D – EA^A. In aggregate, this results in sometimes dramatic underestimations of calculated CT energies. The exact KS potential must obviously yield the correct physics, but it is evidently missing in semi-local functionals. An example from Reference 11 is shown in Figure S1, where TD-KST calculations with the semi-local PBE functional are compared with coupled-cluster calculations. The failure of TD-KST to describe the CT energies is clearly evident.

This problem is inherently related to the wrong asymptotic behavior of approximate KS groundstate XC potentials $V_{\rm XC}$, which should behave as -1/R for an isolated molecule centered at R = 0. For approximate semi-local KS functionals, the asymptotic behavior is related to the lack of integer discontinuities in $V_{\rm XC}$ as the electron number N passes through integers,¹² a feature that the exact KS functional should produce (see next section for more details). Maitra and Tempel analyzed TD-KST CT excitations at large R and showed that the asymptotic $f_{\rm XC}$ should become strongly frequency-dependent to obtain CT and local excitations correctly,¹³ indicating that there is also a connection of the CT problem with the adiabatic approximation. Ziegler and coworkers came to a similar conclusion when analyzing results from a recently developed 'constricted variational' KST approach for calculations of excitation energies.^{14,15} CT excitations are well described in this method¹⁶ even with semi-local functionals, and the calculations possibly mimic the use of a frequency-dependent response kernel in a TD-KST linear response scheme.^{17,18}

One may think of the asymptotic behavior of the potential in the context of the self-interaction error in KST. Consider an N-electron molecule that is neutral (i.e. the sum of nuclear charges

is equal to *N*), and the potential *V* in the Fock operator at a large distance *R* from the center of nuclear charges. In HF theory, the potential is $V_{ne} + V_C$, the sum of the attractive nucleuselectron potential and the total electronic repulsion Coulomb potential, plus an exact exchange (eX) term. Each orbital's contribution to V_C and its self-exchange cancel identically. Further, for large *R* the eX terms involving a given orbital and other orbitals vanishes. Therefore, at large *R* the potential is the positive Coulomb potential of N - 1 electrons, counteracted by the attractive potential V_{ne} of *N* protons, leaving an asymptotic behavior of -1/R. In KST with approximate semi-local XC functionals (excluding any explicit self-interaction corrections), the asymptotic V_{XC} vanishes exponentially with the density at large *R* instead of canceling the electron's non-local self-Coulomb repulsion in V_C , which causes the potential to lack the -1/R asymptote.

The wrong asymptotic behavior of the potential in KST calculations with semi-local functionals unsurprisingly also causes problems with the description of excitations to diffuse states. This deficiency may also have a large impact on response properties that depend on an accurate description of such states. Take, as an example, the 'sum-over-states' (SOS) expression for the isotropic frequency-dependent electric dipole-dipole polarizability,

$$\alpha(\omega) = \frac{2}{3} \sum_{j \neq 0} \frac{\omega_j D_j^2}{\omega_j^2 - \omega^2}$$
(S3)

with ω being the frequency of the perturbing electric field, ω_j an excitation frequency of the system out of the ground state '0', and $D_j^2 = D_j \cdot D_j^*$ the dipole strength calculated from a transition electric dipole moment D_j . For a given approximate form of KST and a given basis set, calculating $\alpha(\omega)$ directly from frequency-dependent linear response equations, or from the right-hand side of Equation (S3) from *all* possible excitations and transition moments obtained from a TD-KST calculation,¹⁹ gives the same numerical answer.²⁰ Therefore an approximation that would lead to a very poor description of an excitation energy or a transition moment in a TD-KST calculation, for a diffuse, CT, or valence excitation, is also detrimental for refractive properties such as $\alpha(\omega)$, optical rotation, and non-linear response.

Shape-corrections^{21–23} to the potential have been devised to deal with the poor description of diffuse states in KST calculations, and to improve the agreement of the HOMO energy with –IP. However, these methods do not offer clear improvements for CT energies and related problems. Hybrid GGA functionals including a fixed (global) fraction $c_{\rm HF}$ of exact exchange (calculated from the KS determinant using the HF exchange functional) may also alleviate the problems to some degree. The coefficient $c_{\rm HF}$ is typically ≤ 0.5 . For example, the eX fraction for B3LYP is 0.2, for PBE0 it is 0.25, and for 'half-half' functionals such as BHLYP rises to 0.5. For a long-range CT excitation one would recover only a fraction $-c_{\rm HF}/R$ of the asymptote in Equation (S1), and the



Figure S1: Calculated lowest CT excitation energy for (*E*)-*N*,*N*-dimethyl-4-(4-nitrostyryl)aniline (DANS = DANS1) and derivatives DANS*n*, with longer bridges (n = 2 - 4). Comparison of an approximate coupled-cluster singles and doubles method (CC2) with TD-KST (PBE functional). The latter severely underestimates the excitation energies. Data from Reference 11.

asymptotic behavior of the potential would not be fully corrected. However, the fraction of eX has a strong influence on the value for $\varepsilon_a - \varepsilon_i$ in Equation (S2). Popular global hybrid functionals such as B3LYP and PBE0 may perform well for CT excitations if the relevant orbitals of the D and A moieties have appreciable overlap. However, typically, the shortcomings of the global hybrid become readily evident in studies of systems with larger D/A separations.¹¹

IP-tuning and DE minimization of RSE hybrids

Range-separated exchange (RSE)

The idea of combining KST with WFT in a way that switches between the two approaches depending on the separation between two electrons, r_{12} , has been around for some time.^{24–26} One motivation is that KST is presumably good at describing dynamic short-range (small r_{12}) correlation, while WFT is good for describing ground states that are inherently of multi-reference character, and ensures correlation at long distance (to obtain vdW interactions), along with the correct asymptotic behavior of the potential of a molecule in a gas-phase.

Range-separation may take different forms. In a commonly applied version one focuses only on the exchange. The electron repulsion r_{12}^{-1} can be split into a short-range (SR) and a long-range (LR) part. Since most molecular quantum-chemistry codes employ Gaussian-type orbital (GTO) basis sets, an error-function based partitioning is frequently adopted for range-separated exchange (RSE) functionals. A commonly used 3-parameter expression from Reference 27 allows to retain global eX and KST fractions of exchange at small and large r_{12} instead of switching between pure approximate KS exchange and pure eX:²⁸

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta \operatorname{erf}(\gamma r_{12})]}{r_{12}} + \frac{\alpha + \beta \operatorname{erf}(\gamma r_{12})}{r_{12}}$$
(S4)

Here, γ is a range-separation parameter. It represents the inverse of a cut-off range around which the exchange functional switches from (predominantly) one type of exchange to (predominantly) another type. Commonly used values for γ in globally parametrized RSE functionals are in the range of 0.3 to 0.5 a.u. For molecular applications, usually the second term on the right-hand side is used for a long-range eX component, while the first term is used for a short-range KS component of the exchange. The parameter α then quantifies the fraction of eX in the short-range limit, while $\alpha + \beta$ gives the fraction of eX in the long-range limit. An asymptotically correct potential of a molecule in the gas-phase requires $\alpha + \beta = 1$ (LC).

When the function $\operatorname{erf}(\gamma r_{12})$, switching from zero to one in Equation (S4), is replaced by $1 - \exp(-\gamma r_{12})$, the exponentially decaying component in the SR part of the range-separation shown in Equation (S5) is known as the Yukawa potential:

$$\frac{1}{r_{12}} = \frac{1 - [\alpha + \beta(1 - \exp(-\gamma r_{12}))]}{r_{12}} + \frac{\alpha + \beta(1 - \exp(-\gamma r_{12}))}{r_{12}}$$
(S5)

This separation was developed for molecular GTO basis calculations by Akinaga and Ten-no.²⁹ It has also been applied in atomic³⁰ and plane-wave type calculations³¹ for the purpose of range-separation. Other types of switching functions can be envisioned as well.²⁹ Seth and Ziegler recently used an exponential form of the range separation of r_{12}^{-1} for a RSE implementation with Slater-type orbital (STO) basis sets.³²

Henderson et al. have even considered a three-way range-separation of r_{12}^{-1} and focused on the importance of eX in the middle range for thermochemistry, reaction barriers, and band gaps.³³ A kind of an 'inverse' range-separation is used, for instance, in the screened hybrid functional by Heyd-Scuseria-Ernzerhof (HSE),^{34,35} which has become popular for calculations of extended periodic systems. Here, the functional has an eX component at short interelectronic distances which is screened at long range. It has been shown that such a functional performs often better for band gaps prediction of extended periodic systems than the HF theory, while at the same time the too small band gaps predicted by non-hybrid functionals are improved significantly. Another approach, currently less well explored, where the fraction of eX in these functional is not constant, is the use of 'local' hybrid functionals. The fraction of eX in these functionals is position- and system-dependent and evaluated based on the kinetic energy density. The interested reader is

referred to References 36 and 37 for details.

For a fully long-range corrected (LC, $\alpha + \beta = 1$) RSE functional, a TD-KST calculation of a CT excitation must produce the correct -1/R asymptotic behavior of Equation (S1) since for large separations of φ_i and φ_a the response kernel switches to the TD-HF form in Equation (S2). Therefore, by design an LC hybrid should produce significant improvements in linear-response TD-KST calculations of CT excitations. This has indeed been found.^{27,38} However, it was noted that a full LC is not always beneficial — at least in functional parametrizations where γ is a fixed predetermined parameter — partially because not every excitation that is labeled CT affords large separations of the orbitals involved.²⁷ A Coulomb-attenuated method (CAM) was proposed accordingly, where the long-range correction is incomplete. For instance, the CAM-B3LYP functional²⁷ uses the range-separation of Equation (S4), with $\alpha + \beta = 0.65$. It was also realized quickly that parametrizations of RSE functionals that are suitable for CT excitations are not necessarily simultaneously useful for other applications such as the determination of atomization energies, molecular geometries or reaction barriers, and the performance of such functionals is sensitive to the choice of α , β , and γ parameters.^{39–50} In particular, a strong dependence of calculated groundand excited-state properties on the range-separation parameter has been revealed.

'One-dimensional' and 'two-dimensional' IP-tuning of RSE hybrids

For global parametrizations of RSE functionals, γ is typically determined by best fits to reference data such as thermochemical properties of a selected molecular training set. However, reparametrization — for example as in the case of the popular CAM-B3LYP functional — for specific purposes or a given class of molecules has been attempted almost as soon as a functional was devised originally. Baer, et al.^{31,51} showed that γ is a functional of the density and should be system-dependent (and density-dependent). Indeed, it was quickly shown that a description of numerous properties / molecules, which are problematic for conventional (TD-)KST, can be improved dramatically using a RSE functional with the range-separation parameter determined individually for a system of interest.^{52–65} More recently it has been stated in no uncertain terms that the use of a global (i.e. system-independent) γ is "doomed to fail dramatically" for larger π conjugated systems, making an optimal tuning procedure "an unavoidable step" when using RSE functionals to study such materials.⁶⁰

Herein, we provide a detailed description of the IP-tuning approach and the minimization of the DE. To illustrate various concepts, calculations were carried out for *para*-nitroaniline (p-NA):



The molecule is a π -conjugated donor = amino / acceptor = nitro (D/A) 'push-pull' chromophore.

p-NA is frequently used in computational studies as a benchmark system for molecular response properties, in particular regarding NLO response. There is a strong physically meaningful π -delocalization that goes along with the 'push-pull' mechanism, and the molecule affords a low-energy CT excitation with a large transition dipole moment in the direction of the N–N axis.

p-NA has previously been considered by us for tuning in Reference 11. Additional results were generated with the Northwest Computational Chemistry (NWChem) package version $6.3.^{66}$ A planar C_{2v} structure for p-NA was taken from Reference 67. The calculations employed a triple- ζ valence polarized (TZVP) Gaussian-type basis set,⁶⁸ along with the functionals PBE^{69,70} and PBE0^{71,72} as well as non-tuned and tuned RSE variants of PBE (vide infra) using the error function partitioning of Equation (S4). HF computations were performed as well. Some calculations employed the CAM-B3LYP functional.²⁷ The NBO 5.0 program⁷³ was used to generate localized orbitals and to analyze the extent of their delocalization.^{74,75} To examine the dependency of the energy on the fractional electron number, a series of single-point energy calculations, using fractional frontier orbital occupations leading to fractional total electron numbers, was performed utilizing a code implemented previously by one of the authors.⁷⁶

An overview of the calculated numerical results, including a variety of energy gaps and a characterization of the amine N π lone-pair (LP) orbital is given in Table S1. The table also lists experimental and calculated reference data available in the literature. Data pertaining to the IP-tuning and the DE are presented in Figure S2, S3, and S4. Figure S5 illustrates the behavior of the energy for fractional-spin states of the p-NA anion as a test for the static correlation error.

Table S1: p-N EA = $E(N)$ –	A: Calc $F(N +$	ulated I - 1), orb	HOMO : ital ener	and LU. røv gan	$\Delta \epsilon = \Delta \epsilon$	ergies (tii Er – Erri	nes – I), - fundamei	—ε _H an(ntal gan	$1 - \varepsilon_{L}, 1$	onization p = IP – EA	otential	IP = E	(N-1)) - E(N)	V), elect st-eners	ron affinity v ontically
allowed electro	mic exc	itation	energy (calculat	ed via	TD-KST	linear re	sponse,	with c	orrespondi	ng oscil	lator st	rength,	f, and	HOMC	-to-LUMO
character, %HI	Chara	cterizati	ion of th	e amine	eΝπΙ	one-pair c	lonor LM	O accol	ding to	an NBO ci	alculatio	n: Occi	upation	of the 'j	parent'	NBO (occ.)
and the percen	tage of t	he LM(3 populi	ation of	2 that	can be att	ributed to	the nit	rogen it:	self (N) and	d the nei	ghborii	ng arom	latic car	bon ato	n (C). ^a
Method		Parameti	rization	<u>—</u> ен	Π		EA	$\Delta \varepsilon$	ΔE_F	ΔE_O	f	%HL	occc.	Contrib	ution	
	Y	α	β											N%	%C	
HF		1.000		8.77	7.16	-1.65	-0.04	10.42	7.20	5.12	0.37	85	1.834	91.7	5.2	
PBE				5.64	8.28	2.80	0.10	2.84	8.18	3.60	0.26	95	1.754	86.5	8.2	
PBE0		0.250		6.64	8.38	2.01	0.21	4.63	8.17	4.13	0.35	76	1.780	87.8	7.6	
LC-PBE0	0.300	0.250	0.750	8.97	8.59	0.09	0.40	8.88	8.18	4.71	0.42	92	1.802	89.0	7.1	
LC-PBE0*	0.214	0.250	0.750	8.56	8.52	0.35	0.32	8.21	8.20	4.54	0.40	94	1.794	88.6	7.3	
LC-PBEh-1	0.000	0.684	0.316	8.45	8.46	0.53	0.49	7.93	7.97	4.84	0.42	93	1.813	89.6	6.8	
LC-PBEh-2	0.025	0.655	0.345	8.46	8.46	0.49	0.46	7.96	8.00	4.80	0.42	93	1.811	89.5	6.8	
LC-PBEh-3	0.050	0.622	0.378	8.47	8.46	0.46	0.43	8.01	8.03	4.76	0.42	94	1.809	89.4	6.9	
LC-PBEh-4	0.075	0.582	0.418	8.48	8.46	0.43	0.41	8.04	8.06	4.72	0.42	94	1.806	89.3	7.0	
LC-PBEh-5	0.100	0.537	0.463	8.49	8.47	0.41	0.38	8.08	8.09	4.68	0.41	94	1.804	89.1	7.0	
LC-PBEh-6	0.125	0.485	0.515	8.50	8.48	0.39	0.36	8.11	8.11	4.64	0.41	95	1.801	89.0	7.1	
LC-PBEh-7	0.150	0.428	0.572	8.52	8.49	0.37	0.35	8.15	8.14	4.61	0.41	95	1.799	88.9	7.1	
LC-PBEh-8	0.175	0.362	0.638	8.53	8.50	0.36	0.33	8.17	8.17	4.58	0.40	94	1.797	88.7	7.2	
LC-PBEh-9	0.200	0.291	0.709	8.54	8.51	0.35	0.32	8.19	8.19	4.55	0.40	94	1.795	88.6	7.3	
LC-PBEh-10	0.225	0.212	0.788	8.56	8.52	0.35	0.31	8.21	8.21	4.52	0.39	94	1.793	88.5	7.3	
LC-PBEh-11	0.250	0.127	0.873	8.58	8.54	0.35	0.31	8.23	8.23	4.50	0.39	94	1.791	88.4	7.4	
LC-PBEh-12	0.275	0.031	0.969	8.60	8.56	0.36	0.31	8.24	8.26	4.47	0.39	94	1.789	88.3	7.4	
Calc. b						0	.84/0.80			4.65/4.66	0.45					
Expt. ^c					8.6		1.1			4.28/4.35						
										÷						

^{*a*} Orbital energies and the various energy gap values in eV. LC-PBE0^{*} = γ -tuned version of LC-PBE0. LC-PBEh-# = a series of α - γ tuned parametrizations of a LC PBE variant.

pVDZ data are 0.69 and 0.62; ΔE_0 : CIS(D)/6-31+G(d)/ EOM-CCSD/6-31+G(d) data, Reference 78, recently values of 4.92 (EOM-CCSD/SVP) and 4.65 ^b Calculated reference data: EA: CCSC(T)/aug-cc-pVTZ / EOM-CCSD/aug-cc-pVTZ vertical detachment energy, Reference 77, the corresponding aug-cc-(EOM-CCSD/SVP+ with a single set of diffuse functions on non-hydrogen atoms) were also reported in Reference 79; f: CIS(D)/6-31+G(d) data, Reference 78. Compare also data in Reference 11.

^c Experimental reference data: IP: vertical ionization energy based on photoelectron spectrum, Reference 80; EA: vertical detachment energy estimated based on photoelectron spectrum, Reference 77; ΔE_0 : gas-phase measurement, Reference 81 based on Reference 82 / vapor phase measurement, Reference 83. An optimal tuning of the range-separation parameter γ in Equations (S4), (S5), or related expressions is easy to perform. The most frequently used approach⁸⁴ is based on the knowledge that in exact KST for a system with N electrons the condition $-\epsilon_H(N) = IP(N)$ should be satisfied.^{7–9} Here, $\epsilon_H(N)$ is the HOMO energy of the N-electron system taken in the limit of approaching integer N from below, and IP(N) = E(N - 1) - E(N) is the vertical ionization potential. With an approximate RSE functional, $\epsilon_H(N)$ and IP(N) have a molecule-specific dependence on the range-separation parameter γ . For a given system, one may therefore justify a non-empirical selection of γ by requiring that⁵¹

$$\epsilon_H(N_0) + \mathrm{IP}(N_0) = 0 \tag{S6}$$

where N_0 indicates the 'normal' electron number of the target system (the electron number of an atom or molecule of interest in its charge state of interest (often neutral)). IP(N_0) is calculated as the difference between the total energy of the systems with N_0 and $N_0 - 1$ electrons. Further, $\varepsilon_H(N_0)$ and IP(N_0) in Equation (S6) are based on the same functional / parametrization. Evaluation of $\varepsilon_H(N_0)$ and IP(N_0) for an array of different range-separation parameters γ , typically between 0 and 0.5 atomic units, reveals quickly which parameter value leads to the condition (S6) being satisfied if at all possible. This γ^* value determines an optimally tuned (IP-tuned, or γ -tuned) RSE functional for a molecule of interest.

The IP criterion (S6) holds for varying electron numbers N for a given external potential (the set of nuclear charges in their chosen positions).⁸⁵ Due to the approximate nature of the functionals used in computations, the same value of γ may not satisfy Equation (S6) exactly for several different N. Following References 53 and 57, one thus may attempt to optimize the IP criterion as best as possible by minimizing⁸⁶

$$J^{2} = \sum_{i} \left[\epsilon_{H}(N_{0} + i) + \text{IP}(N_{0} + i) \right]^{2}$$
(S7)

Since multiply charged states with electron numbers deviating strongly from N_0 can be problematic to deal with, the most commonly applied minimization uses i = 0, 1. In other words, using this criterion the HOMO of the N_0 -electron species and the HOMO of the N_0 +1-electron species are simultaneously IP-tuned to the best degree possible. Modeling of photoionization spectra of organic molecules in Reference 87 required to tune additional orbitals below the HOMO, with good success. Other possible tuning criteria are discussed in References 53, 56, 88, and 89.

Pioneering work on tuned RSE functionals employed fully long-range corrected functionals (LC) with no eX component at $r_{12} \rightarrow 0$, corresponding to $\alpha = 0, \beta = 1$ in Equations (S4) and (S5). In References 76 and 90 we obtained numerical evidence that a range-separated functional may also be successfully IP-tuned for $\alpha \neq 0$ values, but a functional should be fully long-range



Figure S2: p-NA. J^2 of Equation (S7) for $i \in \{0, 1\}$ as a function of the range-separation parameter γ calculated with LC-PBE0 (panel **a**) and CAM-B3LYP (panel **b**). For LC-PBE0, the numerical value of the optimal γ is listed next to the minimum. No minimum of J^2 is found in the case of CAM-B3LYP even for γ values higher than the range shown in panel **a**.

corrected to be tunable for γ in the sense of Equation (S6), i.e. $\alpha + \beta = 1$. This requirement may be related to the finding that accurate continuum (lacking an integer discontinuity) spin-dependent XC potentials should not vanish asymptotically.⁹¹ Rather, one has a generalized Koopmans' theorem $\varepsilon_H^{\sigma}(N) + \mathrm{IP}^{\sigma}(N) = V_{\mathrm{XC}}^{\sigma}(\infty)$ (here, σ is a spin index to distinguish \uparrow from \downarrow orbitals), with $V_{\mathrm{XC}}^{\sigma}(\infty)$ being nonzero. The condition implies that $-\varepsilon_H \neq \mathrm{IP}$, which is certainly what is found numerically with approximate continuum functionals. A nonzero fraction of the DFT exchange potential from a continuum functional in the long-range part of an RSE functional may therefore prevent the IP condition (S6) from being satisfied. In contrast, the correct asymptotic limit of the XC potential afforded by approximate LC RSE functionals by construction, i.e. by switching to 100% eX at large r_{12} is $V_{\mathrm{XC}}(\infty) = 0$, and therefore IP-tuning is possible.

To illustrate the concepts discussed so far, Figure S2 presents calculated values of J^2 of Equation (S7) for two RSE functionals as a function of the range-separation parameter γ for our p-NA example. As expected, for LC-PBE0 with $\alpha = 0.25$, $\beta = 0.75$ an obvious minimum of J^2 is found for $\gamma^* = 0.21$, with $J^2[\gamma^*]$ essentially zero. Therefore, Equation (S6) is satisfied for the HOMO energies of the N_0 and N_0+1 electron species. In the case of the popular CAM-B3LYP functional, which has $\alpha = 0.19$ and $\beta = 0.46$ and therefore switches to only 65% eX at large interelectronic distances, no clear minimum of J^2 is found. As discussed above, this finding may be related to the non-vanishing KS exchange in the limit of $r_{12} \rightarrow \infty$.

The optimal range-separation parameter for p-NA with the LC-PBE0 functional is significantly smaller than typical values of 0.3 to 0.5 a.u. used in global parametrizations of LC functionals. Since γ represents the inverse of a distance, this implies that for p-NA the switch to full eX takes place around a larger interelectronic distance. This is typically found for larger



Figure S3: p-NA. Panel **a**: Energy as a function of fractional electron number ΔN relative to neutral system ($\Delta N = 0$) for selected functionals and HF. Numerical values in parentheses ($C_{<}$, $C_{>}$) provide measures of curvature obtained from fitting quadratic functions to the data sets in the electron-deficient and electron-rich regime, respectively ($\Delta N < 0$, $\Delta N > 0$). Panel **b**: Molecular orbital energies (eV) for HOMO-1 (blue), HOMO (red), and LUMO (green) calculated with ΔN using PBE and optimally α - γ tuned functional LC-PBEh-3. Panel **c**: Isosurface (0.03 a.u.) of amine N lone-pair 'natural LMO'⁷⁴ based on calculations with LC-PBEh-3. The contour plot was taken in a slice approx. 0.5Å above and parallel to the molecular plane with contour values from 0.03 to 1.0 a.u. The numbers listed correspond to occupancy of a parent NBO (Occ.) and percetages of amine N (%N) and neighboring aromatic C (%C) atomic hybrid contributions. LC-3 = LC-PBEh-3 parametrization of Table S2 and Figure S4.

 π -conjugated molecules.^{11,60,64,87,92,93} In systems with spatially more extended conjugation (i.e. π -delocalization occurs over a larger range) the switch to eX with an IP-tuned functional tends to occur at larger interelectronic distances. In fact, the inverse of γ has been associated with the spatial extent of the conjugation.^{60,92} For comparison, $\gamma = 0.3$ to 0.4 a.u. represents a switching distance of about 1.8 to 1.3 Å which brackets the linear extension of a C–C single bond.

Perdew et al. in Reference 7 demonstrated two interconnected properties of KST: (*i*) a linear behavior of the exact total energy versus fractional electron numbers between integers, and (*ii*) a discontinuous change of the local exact KS exchange-correlation potential at integer electron numbers (integer discontinuity). Commonly used approximate exchange-correlation functionals violate these requirements which may cause substantial errors in predicted properties. For instance, as pointed out above the lack of the integer discontinuity is interconnected with the CT problem of linear response TD-KST.¹² Regarding point (*i*), as the exact total energy, $E(N_i + \Delta N)$

varies linearly between integer electron numbers $N_i^{7,94,95}$ the slope of each segment is equal to –IP of the species with integer N_{i+1} electrons.

When the exact energy $E(N_0 + \Delta N)$ is plotted for *negative* ΔN between -1 and 0 the slope is equal to $-IP(N_0)$. For the same molecule, the slope of $E(N_0 + \Delta N)$ with *positive* ΔN between 0 and +1 is equal to $-IP(N_0 + 1) = -EA(N_0)$. At integer N_i , the slope of $E(N_i + \Delta N)$ changes therefore discontinuously unless $EA(N_i)$ and $IP(N_i)$ would happen to coincide numerically. In the following, unless needed for clarity we omit N_0 in the notation and simply write $E(\Delta N)$.

Approximate KST functionals do not generally produce the correct straight-line segment behavior of $E(\Delta N)$ and the discontinuous change in the slope even if they perform well in predicting the energy at integer N_i . Instead, there may be pronounced *curvature* in $E(\Delta N)$ between integers due to the approximations. As Yang & coworkers and others have discussed in detail, the $E(\Delta N)$ curvature is an indication of an unphysical delocalization error (DE) that is related to the oneand many-electron self-interaction problem.^{1,96–98} Positive curvature (referred to by Yang and coworkers as convex behavior, or negative deviation of the $E(\Delta N)$ curve from linear) indicates an unphysical too strong delocalization of the electronic structure. Conversely, negative curvature (concave behavior, or positive deviation of the $E(\Delta N)$ curve from linear) indicates a too strongly localized (not sufficiently delocalized) electronic structure (sometimes referred to as *localization error*). Generally, LDA, GGA, and global hybrid functionals with typical (10 to 30%) fractions of eX produce positive curvature, convex behavior i.e. too strong delocalization, while HF and high magnitude eX-component functionals calculations produce negative curvature, the concave behavior being associated with a too strongly localized electronic system. Recently, a relationship of $E(\Delta N)$ curvature with the lack of integer discontinuities in approximate KST has been noted.⁸⁸ The DE manifests directly in calculated chemical and physical properties of molecules.^{1,98–102} For instance, there is a tendency of approximate density functionals to overestimate the covalent character of dative ligand-metal bonds, or the character of charge-transfer (CT) in the ground state of 'push-pull' organic donor-acceptor π -conjugated chromophores. The DE plays an important role in the aforementioned failure of simple popular functions to describe CT excitations by linear response TD-KST.

As aforementioned, plots of total energies for fractional electron numbers may serve as a very informative diagnostic tool for the DE.^{9,11,54,65,76,88,90,93,96,100–113} Figure S3a shows the energy of p-NA calculated with HF and selected standard functionals for fractional electron numbers, $E(\Delta N)$, with ΔN ranging between -1 and +1. The figure includes additional results that are discussed below. Quadratic fits¹¹⁴ of $E(\Delta N)$ were generated separately in the electron-deficient $(\Delta N < 0)$ and electron-rich $(\Delta N > 0)$ regimes. The coefficients of $(\Delta N)^2$, given as curvatures in the figure, provide numerical measures of the deviation of $E(\Delta N)$ from linearity. The results for p-NA reflect trends that are typically observed in such calculations. Negative curvature (convex

behavior) in the HF calculations indicates insufficient delocalization, i.e. a too strong localization of the p-NA electronic structure. The 'pure' GGA functional PBE produces pronounced positive curvature of $E(\Delta N)$ (concave behavior), which is indicative of over-delocalization. A too strongly delocalized electronic structure arises also from the calculations with the hybrid functional PBE0, but to a lesser degree than with PBE due to the 25% eX component in the functional.

The canonical MOs produced by a KST calculation are delocalized by construction and therefore it is difficult to establish a visual or numerical link of these MOs with the extent of the DE. Localization algorithms can be used to localize the orbitals spatially as best as possible for a given input density matrix. There are molecule-specific limits posed by quantum mechanics as to how well the orbitals of a molecule can be localized, depending on the extent of physically meaningful delocalization and potentially because of the DE. For instance, even in the absence of the DE one would expect that the π orbitals of a delocalized conjugated π -system cannot be fully localized to the one-center lone-pair and two-center bonding 'chemists's orbitals' shown in textbooks. Examples can be found in Reference 115. As demonstrated by Figure S3 and Table S1, the increasing delocalization of the p-NA electronic structure when going from HF via PBE0 to PBE due to the DE, as measured by $E(\Delta N)$ curvature, is reflected in the degree of delocalization of the amine nitrogen π lone-pair orbital represented by the corresponding LMO. A deviation of the occupation of the corresponding NBO from 2 (or 1 for spin-unrestricted calculations) is also a measure of delocalization since the NBOs represent an idealized set of orthonormal one- and two-center orbitals for the system onto which the actual electronic structure is mapped as best as possible. For p-NA, the HF calculation produces a $\pi LP(N)$ LMO with 5% of its density on the neighboring carbon atom of the aromatic ring and the corresponding 1.83 occupation of the idealized N-centered lone-pair NBO. Due to the negative DE we argue that the 5% number is too small and the 1.83 number is too high, i.e. the calculation does not represent the physically meaningful extent of the π -delocalization of p-NA. On the other hand, PBE gives an increase of the carbon percentage to 8% and a drop of the NBO occupation to 1.75. Here, due to the large positive DE the orbital is too delocalized onto the aryl moiety.

For a global hybrid functional, without considering an IP-tuning, a curvature minimization with respect to the fraction of exact exchange has been employed by Sai et al.¹¹⁶ to investigate hole localization in molecular crystals by calculations with periodic boundary conditions. As the $E(\Delta N)$ curvature usually changes sign between HF calculations and a pure GGA functional, an appropriate fraction of exact exchange in a global hybrid minimizing $E(\Delta N)$ curvature systemspecifically ought to be possible in many cases. It has also been noticed that RSE functionals tend to produce low curvature of $E(\Delta N)$ to begin with.^{54,65,96,103,104,107} The observations prompted Yang and coworkers to develop functionals with small DE. The functional parameters were determined to minimize the deviation from the exact linearity condition for the carbon atom and to



Figure S4: p-NA. System-specific tuning of long-range corrected hybrid variant of PBE. Panel a: 3D (left) and contour (right) plot of J^2 (in eV²) as function of α and γ , with $\alpha + \beta = 1$. The thick (orange) line corresponds to $J^2 \approx 0$ along which 12 parametrization were chosen (Table S2). Panel b: Selected corresponding plots of J^2 versus α for a given γ . The numerical values of the optimal α are listed using color code.

provide a good performance for thermochemistry for a molecular test set at the same time.¹⁰⁴ An example is a re-parametrized version of CAM-B3LYP, rCAM-B3LYP with $\alpha = 0.18$, $\beta = 0.95$, and $\gamma = 0.33$. Although rCAM-B3LYP was successfully applied to a number of problematic systems,^{100, 101, 104} it does not necessarily outperform standard RSE functionals.⁹⁸ Vydrov et al.¹⁰³ conjectured that there is always some value of the range-separation parameter for a given RSE functional in such a way that error cancelation leads to a (nearly) straight-line behavior of $E(\Delta N)$. We have demonstrated in References 76 and 109 that such a value may be determined approximately via IP-tuning. Furthermore, as we showed in Reference 90, a combination of system-specific IP-tuning of an RSE functional with simultaneous minimization of the DE can deliver significantly improved performance in ground-state property calculations.

As depicted in Figure S3a, the parametrization of LC-PBE0 with a standard $\gamma = 0.3$ a.u. and $\alpha/\beta = 0.25/0.75$ indeed outperforms HF and both standard functionals, PBE and PBE0, in the sense that the delocalization error for the p-NA molecule is much smaller. The situation improves even further when the IP-tuned system-specific γ value (0.2 a.u.) from IP-tuning is used (LC-PBE0^{*}), resulting in a very small DE. It may already be small enough to ensure a correct description of the electronic structure of the molecule and its properties. However, in some cases, a near-perfect straight-line segment behavior of $E(\Delta N)$ is needed. This leads to the question how to remove a residual DE. The range-separations of $1/r_{12}$ in Equations (S4) and (S5) have 3 unknown parameters. As we are requiring a full long-range correction, this implies $\alpha + \beta = 1$, i.e. $\beta = 1 - \alpha$, which reduces the number of adjustable parameters to two. In Reference 90 we proposed a *two-dimensional tuning* (2DT, α - γ tuning), described here using our p-NA example.

LC-PBEh-#	I	Parametr	ization	J^2	Coefficient	s of $(\Delta N)^2$
	γ	α	β		$\Delta N < 0$	$\Delta N > 0$
1	0.000	0.684	0.316	9.06E-05	0.022	0.015
2	0.025	0.655	0.345	1.63E-05	0.014	0.017
3	0.050	0.622	0.378	7.04E-05	0.001	0.015
4	0.075	0.582	0.418	3.08E-04	-0.005	0.019
5	0.100	0.537	0.463	6.94E-04	-0.014	0.021
6	0.125	0.485	0.515	1.18E-03	-0.020	0.025
7	0.150	0.428	0.572	1.70E-03	-0.027	0.027
8	0.175	0.362	0.638	2.19E-03	-0.029	0.034
9	0.200	0.291	0.709	2.56E-03	-0.033	0.036
10	0.225	0.212	0.788	2.79E-03	-0.035	0.040
11	0.250	0.127	0.873	2.85E-03	-0.037	0.041
12	0.275	0.031	0.969	2.77E-03	-0.035	0.046

Table S2: LC-PBEh parametrizations derived from two-dimensional tuning for p-NA.^a

^{*a*} See also Figures S4 and S3, and compare data from Table S1. γ in a.u., J^2 in eV², coefficients of $(\Delta N)^2$ in eV.

Figure S4a displays the J^2 criterion of Equation (S7) for p-NA obtained with a two-dimensional 11 x 11 grid of α/γ points with α varying between 0 and 1, and γ varying between 0 and 0.5 a.u., with the constraint $\beta = 1 - \alpha$ to satisfy the LC condition, followed by interpolation. The thick orange line in the 'valley' indicates an essentially continuous range of parameter sets for which J^2 is close to zero, while for values of α above approximately 0.7 or γ above approximately 0.28 an IP tuning is not possible (compare Figure S4b). While the exact boundaries depend on the molecule, we have since obtained similar looking plots for a considerable number of other molecules.

Within the *tune-able* α/γ sector, 12 IP-tuned parameter combinations for p-NA were selected as indicated in Figure S4a, and $E(\Delta N)$ plots were generated for each. The parameters, the calculated J^2 based on Equation (S7), as well as the $E(\Delta N)$ curvatures are collected in Table S2. All parametrizations satisfy the optimal tuning criterion to a satisfactory degree (for higher values of α the J^2 are somewhat lower), prompting the question which one should be used? As shown for many examples, calculated ground-state and response properties may be very sensitive to the value of α . Our suggestion in Reference 90 was to select the best tuned α/γ combination by the criterion of the least DE overall as quantified in the curvature values in Table S2. For p-NA, this unambiguously leads to parametrization #3. The 2DT approach is numerically more involved than the simple one-dimensional tuning by an IP criterion alone (1DT, γ -tuning), but it may be necessary for KST calculations of molecular properties that are particularly sensitive to the DE. One of the most representative example, the electric field gradient at the copper nucleus in the CuCl molecule, is discussed in Reference 90. Janak's theorem states that the derivative of the KST total energy with respect to the occupation number of a given orbital is equal to the energy of the orbital.^{9,117} If the orbital in question is the HOMO, it gives relation $dE/dN = \varepsilon_H(N)$. Combined with the straight-line segment behavior of the exact $E(\Delta N)$ this leads to the conclusion that in exact KST, $\varepsilon_H(\Delta N)$ calculated with fractional electron numbers should be constant between integers and adopt the value of -IPof the species with next higher integer N_i . When passing through an integer electron number, there is a discontinuous change in the value of ε_H because the slope of $E(\Delta N)$ and the IP change discontinuously. Part of the discontinuous change of ε_H is simply due to the fact that at integer N_i a different orbital becomes the HOMO. Furthermore, in exact KST the XC potential is supposed to exhibit an *integer (derivative) discontinuity*, such that at integer electron numbers N_i the potential 'jumps' globally by some system-dependent constant amount $\Delta(N_i)$.^{7,118,119} Consequently, it follows that⁷⁻⁹

$$-\varepsilon_{H}^{-}(N_{i}) = \mathrm{IP}(N_{i}) \tag{S8a}$$

$$-\varepsilon_L^+(N_i) = \text{EA}(N_i) \tag{S8b}$$

where in the case of exact KST the value of $\varepsilon_H(N_i)$ is taken in the limit of approaching the integer from below (superscript –), and $\varepsilon_L(N_i)$ is taken as the limit approaching N_i from above (superscript +), due to the integer discontinuity. *L* indicates the LUMO and EA(N_i) = IP(N_{i+1}) is the electron affinity.

 $\Delta(N_i)$ can reach up to several eV, as based on numerical estimates for a variety of systems, ^{120–123} and has crucial physical consequences for a description of fundamental gap, molecular dissociation, charge-transfer excitations, and quantum transport effects.^{1,7,98,118,123–133} An inability to model this phenomenon by continuum XC potentials leads to their nonzero asymptotic limit and the problems with CT excitations as mentioned above. In the absence of a $\Delta(N_i)$, in approximate KST calculations there is no distinction as to from which side the integer N_i is approached in Equations (S8), but the orbital energies may then also represent very poor approximations of IP and EA. This situation is depicted for p-NA in Figure S3b for the PBE functional. The orbital energies vary approximate linearly with ΔN , and at $\Delta N = 0$ (N_0) the orbital energy gap is only about 1/3 of the correct value of IP-EA. The behavior is in stark contrast to the 2DT LC functional LC-PBEh-3. Here, the HOMO energy stays constant between integers, which goes along with the very small $E(\Delta N)$ curvatures, and jumps at N_0 from -IP to -EA of the neutral molecule. The functional is not capable of delivering an integer discontinuity, and therefore the LUMO for $\Delta N < 0$ makes a smooth transition to the HOMO for $\Delta N > 0$. Due to the IP-tuning and the lack of the additional jump in the potential from an integer discontinuity, at N_0 the orbital energy gap represents almost perfectly the calculated $\Delta E_F = IP - EA$, as seen in Table S1. At the same

time, this functional gives an optical gap ΔE_0 (= lowest electronic excitation energy) of 4.76 eV, which is only 0.1 eV above an EOM-CCSD reference value, while PBE0 and in particular PBE significantly underestimate the excitation energy, in part due to its CT character.

An unphysical DE is not the only pitfall of approximate functionals. In References 1 and 134, Yang and collaborators also discussed the static correlation error (SCE), which manifests itself in an incorrect description of degenerate and nearly-degenerate electronic states commonly occuring in transition-metal chemistry, strongly correlated systems, or during bond breaking. Prime examples where problems attributed to the SCE show up therefore include the dissociation of chemical bonds, bonding in metal dimers, or the band structure of Mott insulators and high-temperature superconductors.^{135,136} The concept of SCE has been associated with another condition that the exact KS density functional should satisfy, namely that the total energy for fractional-spin states should be constant and equal to the energy of the corresponding integer-spin states.¹³⁴ A violation of the constancy condition of *E* versus fractional spins is therefore indicative of the SCE. 'Integer' spin and 'fractional' spin refers here to the number of +1/2 and -1/2 electron spins, i.e. in relation to the integrated spin density, not the spin quantum number or spin expectation values.

Figure S5 presents numerical measures of the SCE calculated as a difference between energies for fractional spins and the energy of integer spin state for our example case *para*-nitroaniline. For simplicity, an unpaired electron has been added, and the calculations were performed for the p-NA radical anion. The fractional spin was changed from -1 (zero α -spin (\uparrow), full β -spin (\downarrow) of the unpaired electron, $\langle S_z \rangle = -1/2$) through 0 (0.5 \uparrow , 0.5 \downarrow , $\langle S_z \rangle = 0$) to +1 (1 \uparrow , 0 \downarrow , $\langle S_z \rangle = +1/2$). Due to energetic degeneracy of all the intermediate fractional-spin states, as for example (0.2 \uparrow , 0.8 \downarrow) and (0.8 \uparrow , 0.2 \downarrow), the plots are symmetric around 0.5. The results show that HF and all hybrid functionals give a significant SCE. The smallest SCE is obtained by the nonhybrid PBE functional. These findings match data reported in literature for atoms.^{107,134} The tuned LC functionals, 1DT LC-PBE0* and 2DT LC-PBEh-3, also reveal a significant static correlation error, larger than those for PBE and PBE0. Therefore, while the tuning evidently minimizes the delocalization error there is little benefit in terms of the SCE.

To summarize this section: Suppose that (i) IP-tuning of an approximate RSE hybrid GGA functional by criterion (S7) can be achieved with vanishing J^2 , and (ii) that a parametrization can be found for which the curvature in $E(\Delta N)$ vanishes for ΔN in the range -1 to +1. This implies that $\varepsilon_{\rm H}(N_0 + \Delta N) = {\rm IP}(N_0) = {\rm constant}$ for ΔN between -1 and 0, and $\varepsilon_{\rm H}(N_0 + \Delta N) = {\rm IP}(N_0 + 1) = EA(N_0) = {\rm constant}$ for ΔN between 0 and +1. Since such a functional does not have an additional integer discontinuity, $-\varepsilon_{\rm L}(N_0)$ is then identical to EA(N_0) because the LUMO energy of the N_0 -electron system connects smoothly to the HOMO energy of the system with a fractional extra electron. The HOMO energies for the systems with negative and positive ΔN are constant between $N_0 - 1$ and N_0 , and between N_0 and $N_0 + 1$, respectively. The conditions in



Figure S5: Energy of the radical anion of *para*-nitroaniline relative to the $\langle S_z \rangle = \pm 1/2$ doublet, calculated with fractional spins with a selection of functionals and HF theory. Splines fits were added to guide the eye.

Equations (S8) would then be satisfied exactly, which is part of the reason for the successful treatment of long-range CT excitations with an optimally tuned LC functional. At large separations Rof the donor and acceptor moieties, the approximate form of the CT energy in Equation (S2) for the LC RSE functional corresponds to TD-HF, with the $-[ii|r_{12}^{-1}|aa]$ term being well approximated by -1/R. Together with (S8), one obtains the expected behavior, Equation (S1). Without elimination of residual DE, an IP-tuned functional may not reproduce Equations (S8) exactly. Often, the performance is already good without explicit consideration of the DE for the reason that IP-tuned functionals tend to afford much smaller DEs than GGAs and global hybrids. The two-dimensional tuning introduced by the authors in Reference 90 and outlined above was subsequently adopted by Refaely-Abramson et al.⁸⁷ in order to obtain photo-electron spectra of polyaromatic hydrocarbon molecules that were in excellent agreement with quasi-particle energies from GW many-body calculations.¹³⁷ As demonstrated with the radical ion calculations presented in Figure S5, IP-tuning and DE minimization may go along with an increase of the SCE. Despite this and some other shortcomings^{51, 138} the 'optimal tuning' has attracted much interest, as indicated by an increasing number of publications on this topic.^{11, 18, 89, 92, 93, 108, 110–112, 138–147}

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