

Curvature and Frontier Orbital Energies in Density Functional Theory

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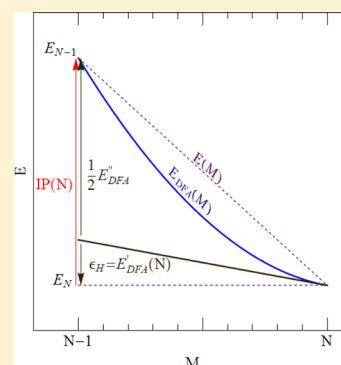
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Supporting Information

ABSTRACT: Perdew et al. discovered two different properties of exact Kohn–Sham density functional theory (DFT): (i) The exact total energy versus particle number is a series of linear segments between integer electron points. (ii) Across an integer number of electrons, the exchange–correlation potential “jumps” by a constant, known as the derivative discontinuity (DD). Here we show analytically that in both the original and the generalized Kohn–Sham formulation of DFT the two properties are two sides of the same coin. The absence of a DD dictates deviation from piecewise linearity, but the latter, appearing as curvature, can be used to correct for the former, thereby restoring the physical meaning of orbital energies. A simple correction scheme for any semilocal and hybrid functional, even Hartree–Fock theory, is shown to be effective on a set of small molecules, suggesting a practical correction for the infamous DFT gap problem. We show that optimally tuned range-separated hybrid functionals can inherently minimize *both* DD and curvature, thus requiring no correction, and that this can be used as a sound theoretical basis for novel tuning strategies.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory



In a seminal article,¹ Perdew, Parr, Levy, and Balduz (PPLB) discovered and proved two properties that exact density functional theory (DFT) must obey. By extending the realm of DFT to fractional electron numbers, using a zero-temperature statistical mixture of integer electron states, they found that: (i) The exact total energy versus particle number curve must be a series of linear segments between integer electron points. Differing slopes of the linear segments reflect discontinuities in the chemical potential, that is, the fact that the electron removal energy is not the same as the electron insertion energy. (ii) Across an integer number of electrons, the exchange–correlation (XC) potential “jumps” by a constant, known as the derivative discontinuity (DD), Δ_{xc} .² Whereas in some cases Δ_{xc} can be small, it is usually sizable.^{3–7} Both properties were originally derived by PPLB to explain how DFT handles the dissociation of heterodimers but were later found to be important in a host of other contexts. Piecewise linearity and its generalization to spin densities were deemed essential to avoiding localization/delocalization and static correlation errors,⁸ and the absence of DD in approximate KS functionals has been implicated in the erroneous description of charge-transfer processes.^{9,10}

The DD has been found to play a decisive and negative role in the relation between the frontier, highest occupied (HOMO), and lowest unoccupied (LUMO) Kohn–Sham (KS) orbital energies (OEs) and the ionization potential (IP) and electron affinity (EA), respectively.³ In principle, with the exact (asymptotically vanishing) KS potential the HOMO

energy can be identified with the IP.^{1,11–15} Potentials derived from approximate functionals that are analytical and therefore do not possess a DD fail to achieve this. Moreover, unless this “missing” DD (MDD¹⁶) is negligible the IP and the EA cannot be *simultaneously* identified with the HOMO and LUMO energies, even with the exact KS potential, leading to the infamous “gap problem”.^{17,18} These conclusions are equally valid for generalized KS (GKS) theory,^{4,19} where a nonlocal potential operator may be present.²⁰

We show that the MDD and the deviation from piecewise linearity are in fact doppelgänger.²¹ The former *necessitates* the latter, and the latter is used to correct for the former and restore the physical meaning of the frontier OEs. We further show that this results in a simple and robust procedure for quantitative correction of these OEs for any underlying KS or GKS DFT. Specifically, optimally tuned range-separated hybrid (RSH) functionals minimize both MDD and curvature, and this may instigate novel tuning strategies.

To establish the notation, we consider Coulomb systems with an average number of electrons equal to $M = N + x$, where N is an integer and $-1 \leq x \leq 0$ is a “fractional hole”. Denoting the total energy of such a system by $E^N(x)$, piecewise linearity dictates that

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Table 1. Calculated PBE, PBE0, and HF OEs ϵ_{H}^N and $\epsilon_{\text{L}}^{N-1}$, End-Point Curvatures $C^N(x)$ ($x = 0, -1$), Average Curvature $\bar{C}^N = \epsilon_{\text{H}}^N - \epsilon_{\text{L}}^{N-1}$, Curvature-Corrected Estimates $I^N(\text{H})$ and $I^N(\text{L})$, and IP obtained from Total Energy Differences, I^N , for a Set of Selected Molecules^a

functional		$C^N(0)$	$C^N(-1)$	\bar{C}^N	$-\epsilon_{\text{H}}^N$	$-\epsilon_{\text{L}}^{N-1}$	$I^N(\text{H})$	$I^N(\text{L})$	I^N	
PBE	F ₂	12.0	12.5	12.3	9.1	21.4	15.1	15.1	15.2	
	N ₂	10.2	10.5	10.4	10.2	20.6	15.3	15.4	15.4	
	NH ₃	10.0	8.8	9.7	5.9	15.6	10.9	11.2	10.9	
	H ₂ O	11.6	10.7	11.5	6.8	18.3	12.6	13.0	12.6	
	CH ₂ O	9.0	9.1	9.2	6.1	15.3	10.6	10.7	10.7	
	HCOOH	8.9	8.7	8.9	6.8	15.7	11.2	11.3	11.2	
	benzene	6.2	5.9	6.0	6.3	12.2	9.4	9.3	9.3	
	naphthalene	4.9	4.9	4.9	5.5	10.4	7.9	7.9	7.9	
	anthracene	4.3	4.2	4.3	5.0	9.2	7.1	7.1	7.1	
	mean deviation from I_N					-4.3	4.3	-0.02	0.08	
	mean absolute deviation from I_N					4.3	4.3	0.05	0.10	
	PBE0	F ₂	8.2	8.6	8.4	11.6	20.0	15.7	15.7	15.8
		N ₂	7.1	7.2	7.3	12.1	19.4	15.7	15.8	15.7
		NH ₃	6.5	5.6	6.3	7.5	13.8	10.8	11.0	10.8
H ₂ O		7.4	6.8	7.3	8.8	16.1	12.5	12.7	12.5	
CH ₂ O		5.8	5.8	5.9	7.8	13.7	10.7	10.8	10.7	
HCOOH		5.5	5.4	5.6	8.5	14.1	11.3	11.4	11.3	
benzene		4.0	3.9	4.0	7.3	11.2	9.3	9.3	9.3	
naphthalene		3.3	3.3	3.3	6.3	9.6	8.0	8.0	8.0	
anthracene		2.9	2.9	2.9	5.7	8.6	7.2	7.2	7.2	
mean deviation from I_N						-2.8	2.8	-0.01	0.07	
mean absolute deviation from I_N						2.8	2.8	0.01	0.09	
HF		F ₂	-4.3	-3.1	-3.7	18.0	14.3	15.9	15.9	16.1
		N ₂	-3.3	-2.7	-2.6	16.8	14.2	15.1	15.5	15.7
		NH ₃	-5.8	-2.8	-4.0	11.6	7.6	8.7	9.0	9.3
	H ₂ O	-7.2	-3.5	-5.0	13.7	8.7	10.1	10.4	10.9	
	CH ₂ O	-5.4	-3.9	-4.9	12.0	7.1	9.3	9.0	9.4	
	HCOOH	-6.3	-3.8	-5.3	12.9	7.6	9.7	9.5	10.0	
	benzene	-2.6	-1.9	-2.3	9.1	6.9	7.8	7.9	8.0	
	naphthalene	-2.0	-1.8	-1.9	7.9	6.0	6.9	6.9	6.9	
	anthracene	-1.8	-1.8	-1.8	7.0	5.2	6.1	6.1	6.1	
	mean deviation from I_N					1.9	-1.6	-0.3	-0.3	
	mean absolute deviation from I_N					1.8	1.6	0.3	0.3	

^aAll values are in electronvolts. All calculations were performed with a development version of NWChem³⁷ using the cc-pVTZ basis and B3LYP/cc-pVTZ optimized molecular geometries.

$$E^N(x) = (1+x)E^N - xE^{N-1} \quad (1)$$

such that the energy of the N and $N-1$ electron systems is given by $E^N = E^N(0)$ and $E^{N-1} = E^N(-1)$, respectively, with the constant slope of $E^N(x)$ equal to the negative of the (vertical) IP of the N electron system, defined as $I^N \equiv E^{N-1} - E^N$. Similar considerations show that as M passes through N , from $N+x$ to $N-x$, the slope jumps discontinuously, from $-I^N$ to $-I^{N+1}$.^{1,19,22} The latter is, by definition, the EA of the N electron system.

Exact KS-DFT maps the fractional charge interacting-electron ensemble onto a noninteracting system with a fractionally occupied HOMO, possessing the same electron density. Remarkably, using Janak's theorem²³ dictates that the energy of the fractionally occupied HOMO is constant: $\epsilon_{\text{H}}^N(x) = (d/dx)E^N(x) = -I^N$.²⁴ As M changes from slightly below N to slightly above N , a new orbital is fractionally occupied, such that $\epsilon_{\text{H}}^{N+1} = -I^{N+1}$. PPLB introduced the DD to argue that $-I^{N+1}$ will usually deviate from $\epsilon_{\text{L}}^N(x \rightarrow 0^+)$ (i.e., just to the left of the N electron point—recall that x is negative), because the KS potential “jumps” by Δ_{XC} . Thus, at integer N , the KS frontier OEs relate to the ionization energies (IEs) as:^{17,25}

$$I^N + \epsilon_{\text{H}}^N = 0; \quad I^{N+1} + \epsilon_{\text{L}}^N = -\Delta_{\text{XC}} \quad (2)$$

so that the KS gap, $\epsilon_{\text{L}}^N - \epsilon_{\text{H}}^N$, and the fundamental gap, $I^N - I^{N+1}$, are related through

$$\epsilon_{\text{L}}^N - \epsilon_{\text{H}}^N + \Delta_{\text{XC}} = I^N - I^{N+1} \quad (3)$$

Numerical estimates for many systems have shown that Δ_{XC} can be as large as several electronvolts.^{5,6} For example, in bulk Si, it is ~ 0.5 eV, which is nearly 50% of the fundamental gap.⁷

Approximate KS functionals, notably local/semilocal functionals used in most DFT applications, typically employ analytical, explicitly density-dependent XC functionals that do not allow for a DD. Almost without exception it is found numerically that ϵ_{H}^N and ϵ_{L}^N obtained from such functionals, respectively, underestimate and overestimate by similar amounts the IP and EA computed from total energy differences using the same functional.²⁵ Explicitly

$$I^N + \epsilon_{\text{H}}^N \approx \frac{1}{2}\delta_{\text{XC}}; \quad I^{N+1} + \epsilon_{\text{L}}^N \approx -\frac{1}{2}\delta_{\text{XC}} \quad (4)$$

where δ_{XC} denotes the deviation between the approximate fundamental and KS gaps:

Table 2. Optimal Value of the Range Parameter γ (in atomic units) in the BNL Functional³² As Determined by Three Different First Principles Tuning Criteria

	Koopmans': $\epsilon_{\text{H}}^N = -I^N$	zero average curvature: $\epsilon_{\text{H}}^N = -I_{\text{L}}^{N-1}$	zero end-point curvature: $C^N = 0$
F ₂	0.73	0.74	0.71
N ₂	0.61	0.61	0.59
NH ₃	0.50	0.51	0.48
H ₂ O	0.57	0.58	0.55
CH ₂ O	0.49	0.49	0.48
HCOOH	0.46	0.46	0.45
benzene	0.31	0.32	0.31
naphthalene	0.28	0.28	0.28
anthracene	0.25	0.25	0.25

$$\epsilon_{\text{L}}^N - \epsilon_{\text{H}}^N + \delta_{\text{XC}} \approx I^N - I^{N+1} \quad (5)$$

One should compare eqs 4 and 5, valid for *approximate*, DD-free KS functionals with eqs 2 and 3, valid in *exact* KS DFT. Consider now that energies from approximate functionals exhibit nonzero curvature, $C^N(x) \equiv (d^2/dx^2) E^N(x) \neq 0$. Let us first approximate $C^N(x)$ as a constant, C^N . The ensemble energy within this (G)KS approximation then deviates from eq 1 and is given by:

$$E^N(x) = \frac{1}{2} C^N x(x+1) + (1+x)E^N - xE^{N-1} \quad (6)$$

From Janak's theorem,²³ the OEs are given by derivatives of the total energy: $\epsilon_{\text{H}}^N = (dE^N(x)/dx)|_{x=0}$ and, for analytical functionals possessing no DD, $\epsilon_{\text{L}}^{N-1} = \epsilon_{\text{H}}^N(x \rightarrow -1^+) = (dE^N(x)/dx)|_{x=-1^+}$. Using these and eq 6 yields $I^N + \epsilon_{\text{H}}^N = 1/2 C^N$ and $I^{N+1} + \epsilon_{\text{L}}^N = -1/2 C^{N+1}$. For perfectly parabolic $E(x)$ curves, then, half the curvature *exactly* corrects for the difference between OEs and IEs. Consequently, the average of the two curvatures *exactly* corrects the gap: $I^N - I^{N+1} = \epsilon_{\text{L}}^N - \epsilon_{\text{H}}^N + 1/2(C^N + C^{N+1})$. In general, $C^N(x)$ does depend on x , but a similar expansion shows that to leading order

$$\begin{aligned} I^N &\approx I^N(\text{H}) \equiv -\epsilon_{\text{H}}^N + \frac{1}{2} C^N(0), \\ I^{N+1} &\approx I^{N+1}(\text{L}) \equiv -\epsilon_{\text{L}}^N - \frac{1}{2} C^{N+1}(-1), \\ I^N - I^{N+1} &\approx \epsilon_{\text{L}}^N - \epsilon_{\text{H}}^N + \frac{1}{2} (C^N(0) + C^{N+1}(-1)) \end{aligned} \quad (7)$$

with the additional exact relation (see the Supporting Information):

$$\bar{C}^N \equiv \int_0^{-1} C^N(x) dx = \epsilon_{\text{H}}^N - \epsilon_{\text{L}}^{N-1} \quad (8)$$

Equation 7 serves as a natural basis for a straightforward "curvature correction" to the OEs of approximate, DD-free density functionals. To study its efficacy, we applied it to PBE calculations of selected small molecules. As shown in Table 1, the negative of the neutral HOMO energy, $-\epsilon_{\text{H}}^N$, and of the cation LUMO energy, $-\epsilon_{\text{L}}^{N-1}$, both deviate by an average of more than 4 eV from the neutral IP obtained from total energy differences, I^N . However, the curvature-corrected estimates, $I^N(\text{H})$ and $I^N(\text{L})$ of eqs 7, are very close to I^N , with absolute mean deviation of less than ~ 0.1 eV.

For simplicity, we have focused our discussion on KS theory. However, piecewise linearity must also be obeyed in GKS theory, that is, even in the presence of a nonlocal potential.^{4,19} The local "remainder potential" of GKS theory,²⁰ which plays a

role analogous to that of the exchange-correlation potential in KS theory, can similarly exhibit a DD.⁴ Therefore, eq 7 is immediately valid for any GKS functional whose "remainder potential" does not possess a DD. The curvature-based correction scheme should therefore apply to any hybrid functional as well, as such functionals are merely a special case of GKS theory.^{3,4,26,27}

Furthermore, Table 1 shows that our correction procedure is indeed equally helpful for the PBE-based global hybrid, PBE0.²⁸⁻³⁰ Here curvatures are somewhat smaller than for PBE and the OEs are closer to I_N . The deviation is still large (close to ~ 3 eV), however. Upon curvature correction, the deviations are essentially eliminated (~ 0.1 eV). Furthermore, the same correction is beneficial even in Hartree-Fock (HF) theory, which itself is just a special case of GKS theory.^{3,20} Indeed, the uncorrected HF gaps in Table 1 are too large. The HF curvatures are negative (implying a *negative* MDD), whereas the curvature-corrected IEs are significantly closer to I_N with a mean deviation of ~ 0.3 eV. This larger deviation is due to a less parabolic $E(x)$, consistent with the larger mean difference between $C^N(0)$ and $C^N(-1)$ in Table 1.

Further insight can be obtained from the following physical arguments. By using an approximate functional devoid of a DD, we deprive the (G)KS potential of its ability to follow the slope change of the ideally piecewise-linear energy versus fractional electron number curve. Concomitantly, for the calculation to be useful at all, we still expect the approximate density functional to deliver rather accurate energies for integer electron numbers. Not unlike nudging an elastic band that is held fixed at regular intervals, this is possible only by introducing curvature. Hence, *compromising on the DD inevitably necessitates curvature*. Conversely, because the curvature must compensate for the MDD, *curvature corrections restore the physical meaning of the (G)KS frontier eigenvalues*. Thus, MDD and curvature are inexorably linked. Equation 8 shows that the difference between the HOMO eigenvalue of the N electron system and the LUMO value of the $N-1$ electron system, which in the exact theory is precisely the DD,^{1,15,18} is *exactly* the average curvature in the approximate theory. Equation 7 fully rationalizes the general similarity between Δ_{XC} of eq 2 and δ_{XC} of eq 4 of the exact and approximate theory, respectively, with the approximate (G)KS gap mimicking the exact one as long as $C_N \approx C_{N+1}$.

The doppelgänger¹⁷ nature of the MDD and the curvature suggests that their coappearance also implies their possible codisappearance: a functional with small MDD will necessarily exhibit small curvature. Recently, we have shown that the MDD can indeed be rigorously minimized, allowing for direct identification of HOMO and LUMO eigenvalues with the IP

and EA. This has been accomplished within a GKS scheme based on a range-split hybrid functional (RSH)³¹ that uses exact nonlocal exchange only for the long-range part of the Coulomb repulsion, $\text{erf}(\gamma r)/r$. The range-separation parameter γ was tuned from first-principles, per system, based on satisfaction of the IP (“Koopmans”) theorem (i.e., the first of eqs 2),^{32,33} as best as possible, for both the neutral and anionic system.^{4,34–36} In Table 2, we show for selected small molecules that tuning γ based on (average or end point) curvature minimization yields optimal γ values similar to those obtained from satisfying the IP theorem for the neutral molecule. In addition, the optimal γ found from one tuning criterion also fulfills the other two criteria to within ~ 0.05 eV, that is, to within the above-obtained accuracy of curvature corrections.

The above argument explains the hitherto heuristic observation that optimally tuned RSHs tend to have small curvature^{4,38,39} and provides a solid theoretical framework for more elaborate RSHs, where both the range-separation parameter and the short-range exact-exchange fraction are tuned by demanding minimization of both MDD and curvature.^{40–43}

Tuning using end-point curvature is additionally advantageous in that it may be performed entirely on the original system, without recourse to its fully or partially ionized states, a major advantage for solids where ionization is more challenging owing to periodic boundary conditions. This can be accomplished by combining Janak’s theorem with the definition of curvature, yielding $C_N = \partial_{\epsilon_n}(N)/\partial f_H$ and $C_{N+1} = \partial_{\epsilon_L}(N)/\partial f_L$. Treating orbital occupation as a perturbation, we present in the Supporting Information a linear-response equation³³ whose solution includes the curvatures $\partial_{\epsilon_n}/\partial f_n$ with respect to any KS orbital ψ_n . Starting from an analogue of the single-pole approximation in linear-response time-dependent DFT,⁴⁴ we also derive an order-by-order expansion for the curvature. The zero-order estimate for the curvature (see also ref 33) equals the OE correction estimate of ref 45. However, we demonstrate, using H₂O, that this bare “self-interaction” term grossly overestimates curvature because of extensive relaxation entering in higher orders, even beyond second.

In recent years, several schemes for curvature-minimizing orbital-specific corrections of (semi-) local functionals have been put forth (e.g., refs 46–50). Because curvature minimization *must* be accompanied by a mechanism for MDD reduction, these are useful only if the MDD-curvature equivalence can be overcome. These schemes achieve this by formally departing from the (G)KS framework because different orbitals are subject to different potentials – an approach different from ours.

A prevalent view is that self-interaction errors cause curvature and therefore self-interaction corrections remove it, yet it was already noticed that functionals that are formally one- and two-electron self-interaction-free can still deviate from piecewise linearity,¹⁹ leading to the suggestion that the curvature can be identified with the “many-electron self-interaction errors (SIEs)”. Our approach is to interpret curvature as required by MDD. Self-interaction is then just a mechanism for creating the required curvature. Other mechanisms are possible. Indeed, curvature can also arise in functionals that are formally self-interaction free, such as HF.

In conclusion, we have shown analytically that the absence of a DD and deviation from piecewise linearity are, quantitatively, two sides of the same coin. We have shown how curvature can

be used to estimate quite accurately the MDD and to estimate the deviation of the frontier OEs from the IP and EA. As a special case, we showed that optimally tuned RSHs designed to minimize the DD and bring the OEs close to the corresponding IPs must also mitigate curvature. This allowed us to suggest the minimization of curvature obtained from a linear-response-like formalism as a tuning criterion and to examine its relation to one-electron self-interaction errors. Importantly, all claims were established quantitatively using a set of small molecules and selected semilocal, hybrid, RSH, and HF calculations.

■ ASSOCIATED CONTENT

📄 Supporting Information

Definition of the missing derivative discontinuity, detailed mathematical developments concerning the calculation of curvature from a self-consistent calculation and a closed shell simplification, and finally comments on finite temperature effects. This material is available free of charge via the Internet <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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