Vertical Ionization Energies, Generalized Kohn-Sham Orbital Energies, and the Curious Case of the Copper Oxide Anions

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Abstract

Are the vertical ionization energies from a bound electronic system, initially in its ground state, equal to minus the corresponding exact Kohn-Sham orbital energies of density functional theory (DFT)? This is known to be true for the first or lowest vertical ionization energy. We show that the correction from time-dependent DFT arises from the continuum and need not vanish. Recent work compared the experimental photoemission thresholds of the molecules Cu_2O-, CuO^-, CuO^-_2 , and CuO_3- with minus the corresponding orbital energies from a generalized gradient approximation (GGA) and its global and range-separated hybrids with exact exchange, finding striking differences which were attributed to self-interaction error, strong correlation, or both.

Here we extend that work to include the local spin density approximation (LSDA), its Perdew-Zunger self-interaction correction with Fermi-L¨owdin localized orbitals (LSDA-SIC), a quasi-self-consistent locally scaled-down version of LSDA-SIC (QLSIC), and the

Quantum Theory Project QTP02 range-separated hybrid functional, all but LSDA implemented in a generalized Kohn-Sham approach. QTP02 impressively yields a near equality for many *sp*-bonded molecules. But, for the copper oxide anions studied here, none of the tested methods reproduces the experimental photoemission thresholds.

Introduction

A vertical ionization energy is the work to move an electron from a bound system in its ground state to the bottom of the energy continuum, without relaxation of the nuclear positions.[1] If the system is a single atom, there is no distinction between vertical and adiabatic ionization. The smallest vertical ionization energy is a ground-state energy difference at fixed external potential for the electrons, while the others are single-hole ionization (excitation) energies. The vertical ionization energies are measured in a photoemission spectrum.[2] For a molecule

or solid, the spectral thresholds are broadened by the nuclear vibration.

Work done prior to and in 1984 established[3,4] that the smallest vertical ionization energy equals minus the exact Kohn-Sham[5] energy eigenvalue for the highest-occupied orbital. (The exact Kohn-Sham potential is an effective potential that, acting on non-interacting electrons, reproduces the exact ground-state electron density of the real interacting system.) An early numerical construction of nearly-exact Kohn-Sham potentials for the spherical atoms He, Be, Ne, and Ar by Zhao, Morrison, and Parr[6] supported this theorem for the first ion-

ization energy. Computationally-efficient local or semi-local approximations to the density functional for the exchange-correlation are far from satisfying this ionization potential theorem, due to spurious self-interaction,[2,7–9] but hybrid functionals that mix in a fraction of exact exchange are capable of satisfying it approximately, especially with optimal materialdependent tuning,[10] in which a parameter in the functional is adjusted for each system for

internal satisfaction of this first ionization potential theorem.

Are the other vertical ionization energies also equal to minus the corresponding exact Kohn-Sham orbital energies?[11–13] There is numerical evidence that, for normally correlated atoms and molecules with only *s* and *p* electrons, there is at least an approximate equality. Chong, Gritsenko, and Baerends[11] have made numerical and theoretical arguments for an approximate equality, that is closer for ionization from valence levels than from core levels. Table 1 compares the results of refs 6 and 11 for He, Be, Ne, and Ar with each other and with measured vertical ionization energies provided in refs 6, 11, 14, and 15.

Bartlett, Lotrich, and Schweigert[12,13] have given a formal argument for an equality, based on a time-dependent density functional theory (TDDFT):[16] Let the electron be removed from an initially occupied orbital i and moved to an initially unoccupied orbital a. Then, as a approaches the top of the Rydberg series ($\epsilon_a = 0$), the matrix elements that additively correct the orbital energy difference $\epsilon_a - \epsilon_i$ tend to zero. In the Appendix, we argue that, in a careful treatment of the correction from continuum or unbound Kohn-Sham orbitals, the correction itself need not vanish.

In 2018, Shi, Weissman, Bruneval, Kronik, and Ogut[17] made some comparisons of approximations with the measured photo-electron spectra[18,19] of the molecular anions Cu_2O^-, CuO^-, CuO^-_2, and CuO^-_3. The first three had been studied earlier by the sophisticated equation of motion coupled-cluster (EOM-CC) method,[20,21] which reasonably matched the experimental spectra for at least the first two strongly correlated molecules. Ref 17 computed Kohn-Sham orbital energies with the PBE generalized gradient approximation to the exchange-correlation energy, the PBE0 global hybrid of PBE with 25% of exact exchange, two optimally tuned range-separated hybrids (OT-RSH) with full exact exchange at long range, and the G_0W_0 quasi-particle corrections to PBE0 and BHLYP. Because PBE orbital energies can actually be positive for small negative ions (bound only by the use of a localized basis set for the orbitals), ref 17 shifted the first PBE peak to match the PBE change of ground-state

total energy. None of these approaches agreed with experiment very well, a result that the authors suggested might arise from self-interaction error[7–9,22] (partly corrected by the hybrid functionals) and strong correlation (uncorrected by the hybrids).

Table 1: Comparison of numerical "exact" Kohn-Sham orbital energies for spherical atoms from ref 6 (ZMP) and ref 11 (CGB), which agree well with one another and with experimental vertical ionization energies cited in those articles or in refs 14 or 15. The agreement with experiment is very close for valence orbitals, and not so close for 1*s* core electrons. Relativistic effects are included in the experimental values, but are expected to be very small for these atoms and orbitals. All energies in eV. (The experimental values for Ne 1*s* are properly gas phase. The experimental value for Be 1*s* from ref 14 is for excitation to the Fermi level of solid Be. Our value in parentheses approximately corrects that value by twice the work function of Be (3.9 eV), a procedure that gives a useful correction for 1*s* removal from Ne implanted[15] in solid Cu, Ag, and Au).

Atom	orbital i	$-\epsilon^{\mathrm{ZMP}}{}_i$	$-\epsilon^{\mathrm{CGB}}{}_i$	Expt
He	$1s$	24.6	-	24.6^{6}
Be	$2s$	9.2	9.3	$9.3^{6,11}$
	$1s$	114.7	122.3	$111.8^{14}(119.6)$
Ne	$2p$	21.5	21.6	$21.6^{6,11}$
	$2s$	44.7	44.8	-
	$1s$	838.4	838.5	$870.3,^{11}\ 870.4^{15}$
Ar	$3p$	15.2	-	15.8^{6}

In this work, we extend their results to several more functionals: the local spin density approximation (LSDA),[5,23] two self-interaction corrections to LSDA,[24,25] and Bartlett's QTP02 long-range-corrected hybrid.[13]

LSDA was the first approximation to the density functional for the exchange-correlation energy. The Perdew-Zunger self-interaction correction[22] to LSDA (LSDA-SIC), using FermiLo¨wdin localized orbitals[24] that minimize the total energy, is exact for all one-electron densities and has been applied here self-consistently. It is known to overcorrect LSDA in regions where the electron density varies slowly over space, so we have also tried a locally-scaleddown self-interaction correction (QLSIC),[25] which is exact for all one-electron and all

uniform densities, and is implemented here quasi-self-consistently,[26] using the same local scale-down

factor for the SIC term in the effective potential as for the SIC term of the energy density. All methods studied in our work except LSDA have been implemented in a generalized Kohn-Sham approach, in which the effective potential for an orbital-dependent functional is not constrained to be a function of position *r* alone. For LSDA, we have shifted the first peak of the computed spectrum to agree with the corresponding difference of ground-state total energies. This shift is strongly needed for LSDA, as for PBE. For the other tested functionals, we put a vertical hash mark on the horizontal axis to show the corresponding

total energy difference for the first vertical ionization energy.

The QTP02 functional from the Quantum Theory Project[13] is also a range-separated hybrid with full exact exchange at long range. That feature is correct in atoms and small molecules, but not in solids where the needed fraction of exact exchange at long range is the inverse of the bulk dielectric function,[27] a global material-dependent parameter (which

vanishes in a metal). The LYP correlation in QTP02 is also incorrect for metals. The QTP02 parameters are not material-dependent but are determined using conditions that for a hybrid functional are implied by a correct linear variation[3] of the total energy as a

function of fractional average electron number[28,29] in the system between any two adjacent integers (an effect observed for SIC-LSDA,[22] but not for LSDA, before its exact derivation in ref 3). Because the linear variation cannot be achieved exactly for all systems by a hybrid functional with a finite number of parameters, two parameters were trained on a few small molecules, including some that contain a 3*d* atom. Tests on eleven small organic molecules have demonstrated that minus the occupied QTP02 orbital energies are impressively close to reference vertical ionization energies with a mean absolute deviation of 0.36 eV in Table IV of ref 13.

Computational details

The LSDA, LSDA-FLOSIC, and quasi-self-consistent LSIC calculations were performed using the UTEP-NRLMOL-based FLOSIC code.[30–34] All calculations are spin-unrestricted and no symmetry constraints are placed during FOD optimization. The FOD force tolerance is set to 5×10^{-4} Hartree/Bohr and an energy convergence criterion of 10^{-6} Hartree is chosen. To better describe the diffuse valence electrons of the anionic molecules considered, the standard NRLMOL basis set was supplemented with an additional *s*-type, *p*-type, and *d*-type even-tempered bare Gaussian.[35] QTP02 calculations were performed in the PySCF code.[36] The energy tolerance was set to 10^{-7} Hartree and the aug-cc-pvqz basis set[37] was used. Since ref 17 found that the photoelectron spectra were insensitive to the difference between PBE and PBE0 bond lengths and bond angles (Fig. 1 of ref 17), we used the PBE0 geometries from ref 17.

Results and discussion

Figures 1–4 show our results for Cu_2O^-, CuO^-, CuO^-_2, and CuO^-_3, respectively. The top panel is the experimental spectrum,[17–19] with its natural vibrational broadening. The next four panels are based on our calculated LSDA, LSDA-SIC, QLSIC, and QTP02 orbital energies, as explained in Section . The computed lines have been arbitrarily broadened by Gaussian functions of width 0.1 eV, as in ref 17. The LSDA (but not the other) orbitalenergy spectra have been shifted as described in Section . The upper limit of the plotted binding energy has been extended beyond that in ref 17 to show more of the calculated spectra. We have used the same total spin as in ref 17, whether or not it is a ground state for a given functional. For example, for CuO^-_2, we use the triplet, which is the ground state in LSDA and QTP02, although the singlet is the ground state in LSDA-SIC and QLSIC.

We do not see many consistent patterns in these figures. One is that, while the LSDA

highest-occupied orbital energy is positive in three of the four figures and negative but small for CuO^{-}_{2}, which would put the first LSDA peak far too low compared to the experimental one, the energy shift that brings the first peak into agreement with the LSDA energy difference often places the LSDA first peak above the experimental one. This implies that a full correction of the LSDA total energy would lower the ground-state energy of the neutral more than it lowers the energy of the anion. The shifted LSDA spectra resemble the shifted PBE spectra in ref 17.

The LSDA (and PBE) spectra do not show large energy gaps between peaks. The self-

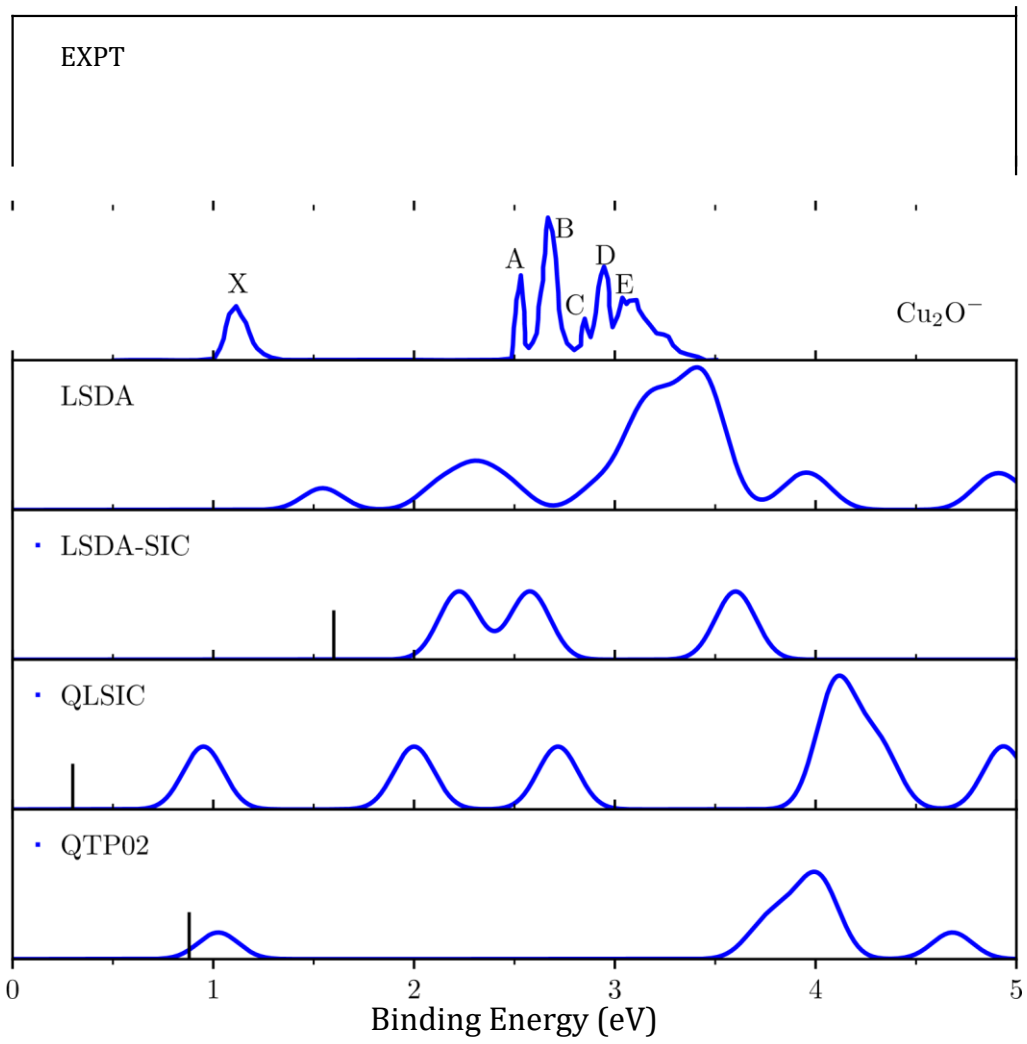
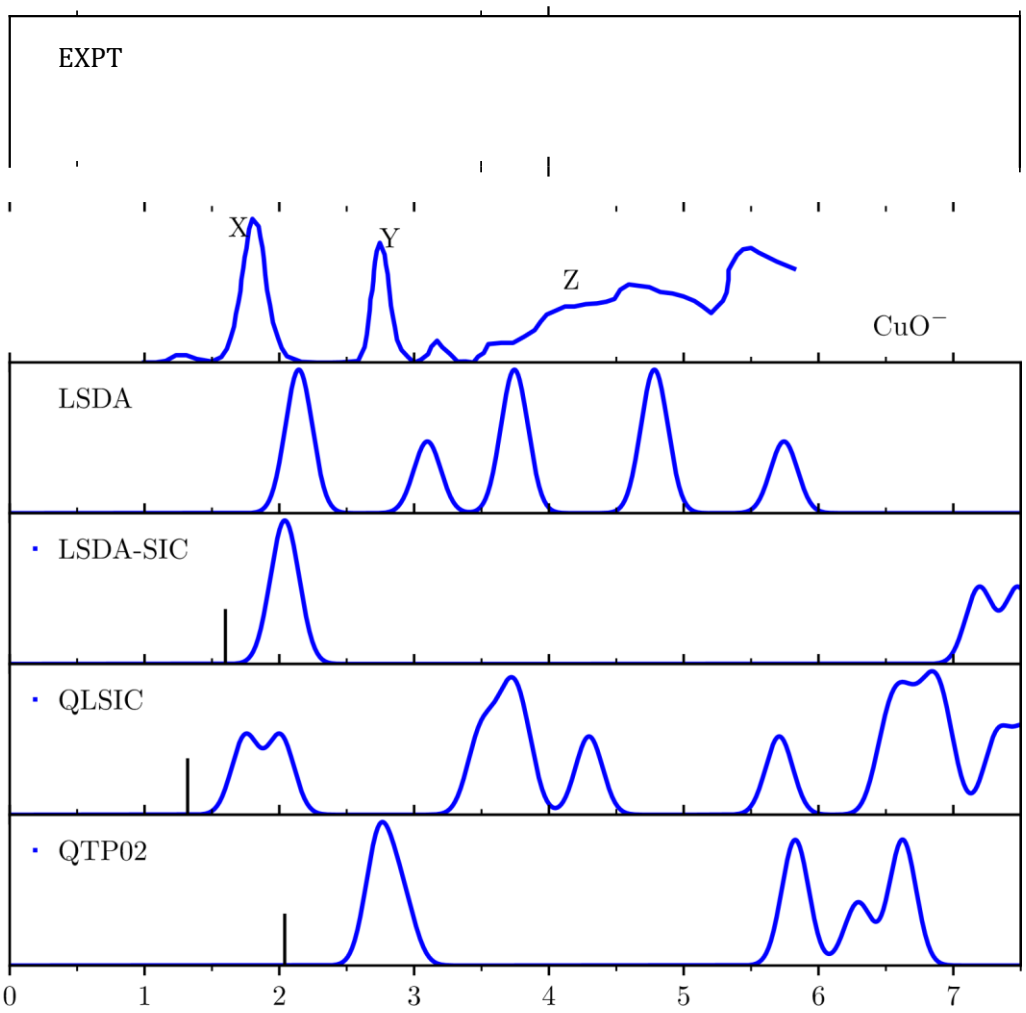


Figure 1: Cu_2O^- photoemission vertical ionization energies versus minus occupied orbital energies computed from LSDA, LSDA-SIC, QLSIC, and QTP02 density functionals, with vibrational broadening for the experimental values and artificial broadening for the computed values. The LSDA spectrum has been shifted to put its first peak at the corresponding LSDA ground-state total energy difference. For the other functionals, a vertical hash mark shows the corresponding ground-state energy difference.

interaction corrections and the hybrid functionals tend to open gaps, which are sometimes but not always present in the experimental spectra.

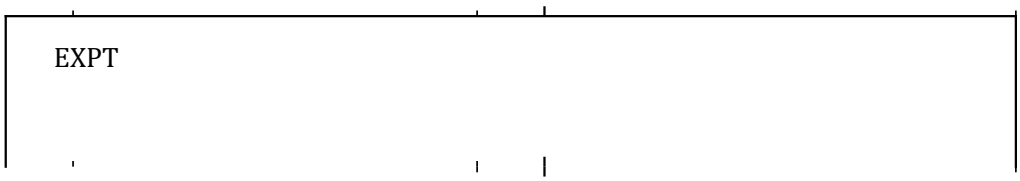
The LSDA-SIC results are unusually erratic, and especially in CuO^-_3, where Fig. 4 shows a huge 4 eV difference between the first peak calculated from the orbital energy and from the total energy difference. Figure 5 shows how the peaks for CuO^- shift around as the global



fraction of SIC is scaled up from 0% to 100%. In this figure, unlike the previous ones, all calculated spectra have been rigidly shifted to make the first peak equal to the corresponding total energy difference.

Binding Energy (eV)

Figure 2: CuO^- photoemission vertical ionization energies versus minus occupied orbital energies computed from LSDA, LSDA-SIC, QLSIC, and QTP02 density functionals, with vibrational broadening for the experimental values and artificial broadening for the computed values. The LSDA spectrum has been shifted to put its first peak at the corresponding LSDA ground-state total energy difference. For the other functionals, a vertical hash mark shows the corresponding ground-state energy difference. The very weak first peak in the experimental spectrum has been interpreted recently as evidence for a long-lived triplet excited state.[38]

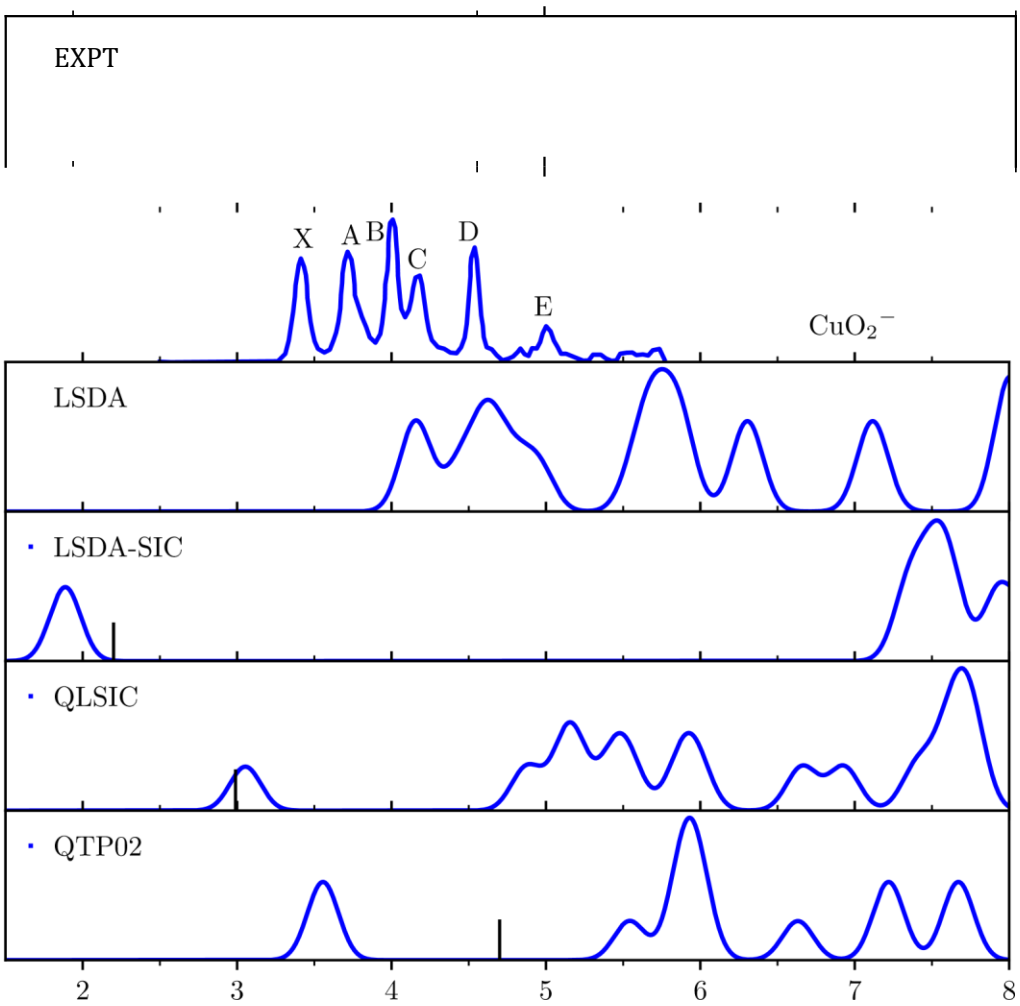


The first peak in QLSIC is far too low in Cu_2O^- in comparison with the experimental first peak. While QLSIC is rather accurate for many total energies and energy differences in *sp* systems, it radically underestimates hydrogen and weak bonds.[39] These results suggest the need to find a better way to locally scale down the full self-interaction correction in many-electron regions. A more correct local scaling is now under development.[40]

The QTP02 range-separated hybrid, which predicts orbital energies in many organic molecules in close agreement with measured vertical ionization energies, does not do the

Binding Energy (eV)

Figure 3: CuO^-_2 photoemission vertical ionization energies versus minus occupied orbital energies computed from LSDA, LSDA-SIC, QLSIC, and QTP02 density functionals, with vibrational broadening for the experimental values and artificial broadening for the computed values. The LSDA spectrum has been shifted to put its first peak at the corresponding LSDA ground-state total energy difference. For the other functionals, a vertical hash mark shows the corresponding ground-state energy difference.



same for the copper oxide anions. Although it is a range-separated hybrid with 100% of exact exchange in the long range, like OT-RSH(α = 0.2) of ref 17, QTP02 gives rather different results, and in CuO^- and CuO^-_3 its highest occupied orbital energy seems far too negative.

To test the implementation of QTP02 in the libxc library and PySCF code that we used, we computed the QTP02 highest occupied orbital energies for 16 small organic molecules (the ones for which we could find reliable geometries) from Table S5 of Haiduke and Bartlett:[13] H_2O, CO, HF, N_2, F_2, CH_4, HCN, SiO, HCl, P_2, CS, CCl_4, SiF_4, CO_2, NH_3, and $CFCl_3$.

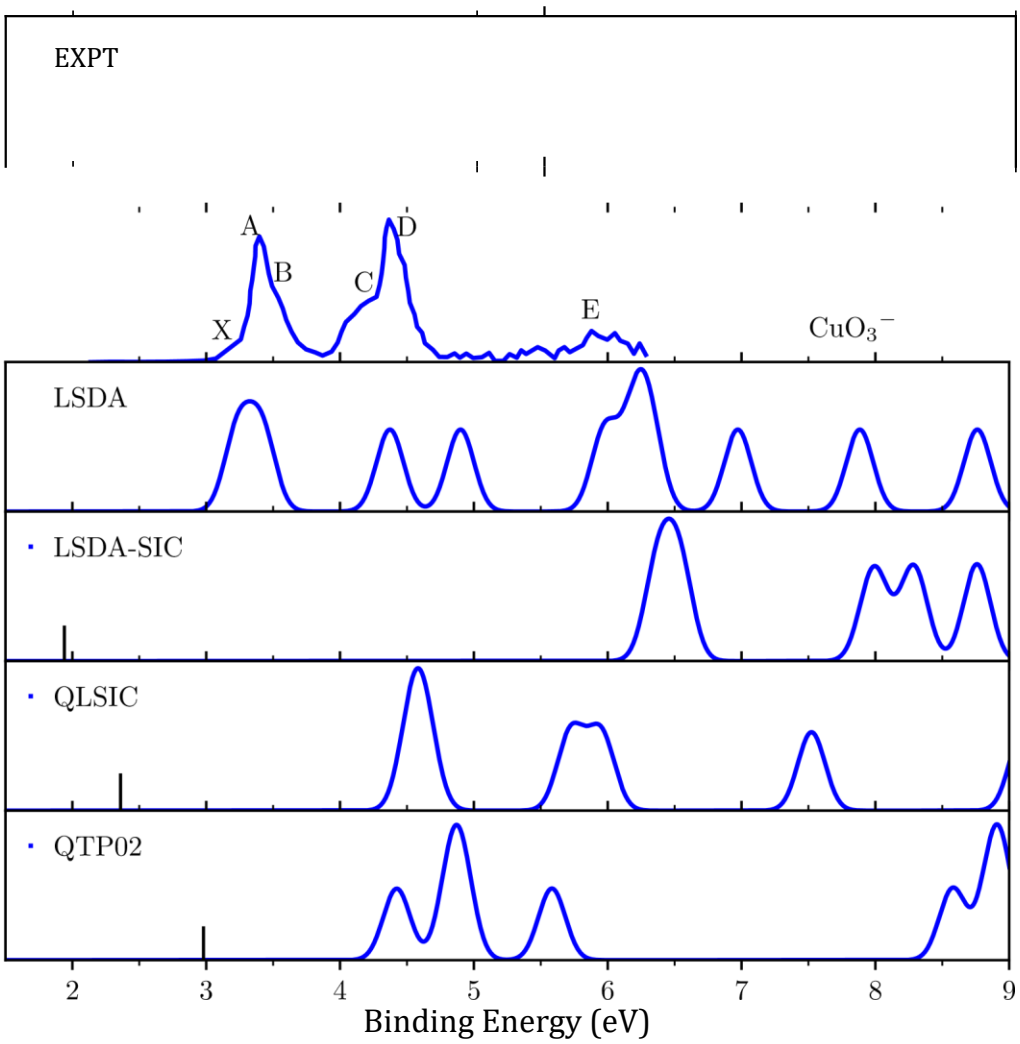


Figure 4: CuO^-_3 (isomer2, see Fig. 11 of ref 17) photoemission vertical ionization energies versus minus occupied orbital energies computed from LSDA, LSDA-SIC, QLSIC, and QTP02 density functionals, with vibrational broadening for the experimental values and artificial broadening for the computed values. The LSDA spectrum has been shifted to put its first peak at the corresponding LSDA ground-state total energy difference. For the other functionals, a vertical hash mark shows the corresponding ground-state energy difference.

The mean absolute deviation was 0.06 eV, and the mean absolute relative deviation was about 0.5%. Thus we believe that QTP02 has been implemented correctly.

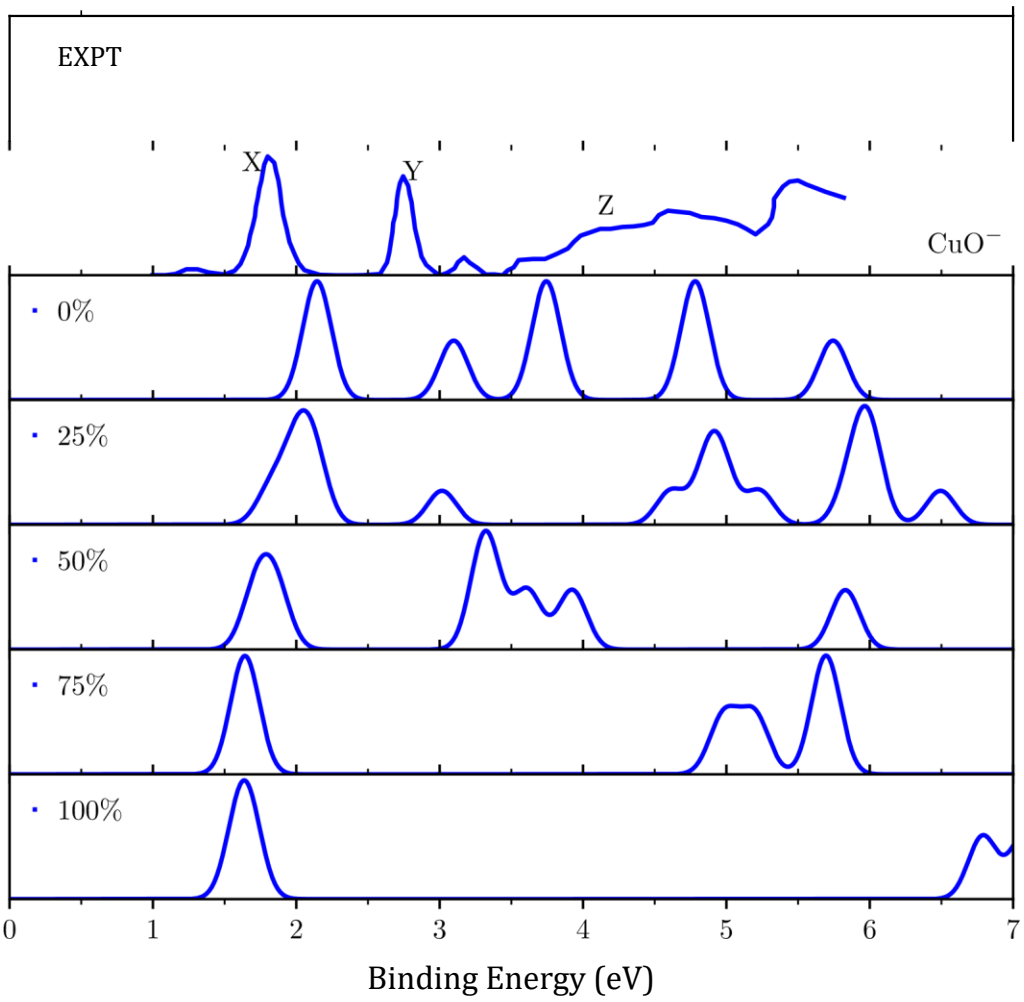


Figure 5: How the LSDA-SIC peaks for CuO- shift with the global fraction of full SIC, as it increases gradually from 0% (the LSDA curve of Fig. 2) to 100%, Unlike in Figs. 1–4, all calculated spectra have been rigidly shifted to position the first peak at the corresponding total-energy difference.

Conclusions

The first vertical ionization energy equals minus the highest-occupied exact Kohn-Sham orbital energy, although this condition is poorly satisfied by LSDA and PBE and the improvement from SIC and hybrid functionals is not as reliable in the copper oxide anions as might have been hoped. The most consistent improvement in the satisfaction of this constraint comes from OT-RSH(α = 0.2), and then at the price of a material-dependent

parameter.

For all vertical ionization energies, the total energy differences[41] from good generalized gradient approximations (GGAs) and meta-GGAs are expected to be reasonably good approximations, and certainly much better than their orbital energies. For the functionals tested here, the most successful total energy differences were from LSDA.

The extension of the orbital-energy theorem to all vertical excitation energies neglects the probably non-zero but possibly small correction of time-dependent DFT from the continuum that we have found in the Appendix. The extension seems to be approximately true in many *sp* atoms and molecules. It is not clear if it is even approximately true in the copper oxide anions. One way to check this might be to compute an accurate electron density for CuO^- (38 electrons), and then make an accurate Kohn-Sham inversion (as in ref 42) to find an
almost-exact Kohn-Sham potential and orbital energies.

No tested density functional approximation so far has produced even a good approximation to this extension in the four copper oxide anions. ref 17 described the transition-metal oxides as "stringent test cases for state-of-the-art computational methods", and for all we
know the copper oxide anions may be among the most stringent cases.

The disappointing performance of LSDA-SIC and LSIC is not without precedence, The overcorrection of LSDA by SIC (with real Fermi-L¨owdin localized orbitals) leads to unphysical results in the Cu atom,[43] the Cr atom,[43,44] and the Cr dimer[44] The way that LSIC scales down the self-interaction correction in many-electron regions can lead to its own large errors.[39]

This subject can be revisited as better self-interaction corrections[40] and hybrid functionals (both fully nonlocal functionals of the occupied Kohn-Sham orbitals) are developed.

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Appendix: Vertical Ionization Energies in TDDFT

Suppose we have a ground-state of interacting electrons, and want to compute the excitation frequency ω_{ia} from an occupied orbital i to an unoccupied orbital a. The frequency for a noninteracting ground state of the same electron density is the Kohn-Sham orbital energy difference $\omega_{\mathrm{KS}ia} = \epsilon_a - \epsilon_i$ (in atomic units). We must solve the Casida equations[45,46]

$$\sum_{a'} \Omega_{ia,ia'}(\omega_{ia}) v_{ia'} = \omega_{ia}^2 v_{ia} \tag{1}$$

$$\Omega_{ia,ia'}(\omega_{ia}) = \omega_{\mathrm{KS}ia}^2 \delta_{a,a'} + 2(\omega_{\mathrm{KS}ia}\omega_{\mathrm{KS}ia'})^{1/2} < ia | f_{\mathrm{H}xc}(\omega_{ia}) | ia' > \tag{2}$$

Here, the matrix element (between products of Kohn-Sham orbitals) of the Hartree exchangecorrelation kernel $f_{\mathrm{H}xc}$

$$< ia | f_{\mathrm{H}xc}(\omega_{ia}) | ia' > = \int\int d^3r\, d^3r' \phi_i(r) \phi^*_a(r) f_{\mathrm{H}xc}(r, r', \omega_{ia}) \phi^*_i(r') \phi_{a'}(r') \tag{3}$$

of the interacting system provides the needed correction to $\omega_{\mathrm{KS}ia}$. Unless we neglect the frequency dependence of the kernel (adiabatic approximation), the excitation frequency must be found by iteration. All unoccupied states including the continuum[47,48] or unbound states with $\epsilon_{a'} \geq 0$ are included in principle. (In a practical calculation with localized basis functions, this is achieved by using a large and flexible basis set.)

To find the vertical ionization energies, we let a approach the top of the Rydberg series or the bottom of the continuum ($\epsilon_a = 0$). We can think about a limiting process in which the system is confined near the center of a sphere whose volume V goes to infinity at the end of the calculation. Since $\phi_a \sim V^{-1/2}$, the correction to $\omega_{\mathrm{KS}ia}$ from each a' tends to zero as $V \to \infty$, but the continuum contribution need not tend to zero even though it also has $\phi_{a'} \sim V^{-1/2}$, since the sum over a' up to any fixed positive continuum energy gives a contribution from the Hxc kernel of order $V(V^{-1/2})^2 = V^0$. The same effect is familiar in the calculation of the electron density of a uniform noninteracting electron gas: Each occupied plane wave contributes a term of order $(V^{-1/2})^2$) to the electron density, but the sum over plane waves up to the Fermi energy gives a density of order $V(V^{-1/2})^2 = V^0$. Thus in the vertical ionization energy from a bound state i there is a correction to $-\epsilon_i$ from the continuum that need not vanish even for the exact Kohn-Sham orbitals and orbital energies.

Author contributions

CS and RM are co-equal first authors. AR and JPP designed the work and wrote the first draft. CS, RM, and JN performed the calculations and contributed to the design and writing. GIC contributed to the design of the project.

Dedication

AR and JPP dedicate this article to our good friend and collaborator on many research projects. Professor Gustavo Scuseria, whose work has had great impact across chemistry and condensed matter physics, both in coupled cluster theory and in density functional theory.

References

(1) McKechnie, S.; Booth, G. H.; Cohen, A. J.; Cole, J. M. On the accuracy of density functional theory and wave function methods for calculating vertical ionization energies. *J. Chem. Phys.* **2015**, *142*, 194114 1–8.

(2) Ko¨rzdo¨rfer, T.; Ku¨mmel, S.; Marom, N.; Kronik, L. When to trust photoelectron spectra from Kohn-Sham eigenvalues: The case of organic semiconductors. *Phys. Rev. B* **2009**, *79*, 201205–201209.

(3) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz Jr, J. L. Density-functional theory for fractional particle number: Derivative discontinuities of the energy. *Phys. Rev. Lett.* **1982**, *49*, 1691–1694.

(4) Levy, M.; Perdew, J. P.; Sahni, V. Exact differential equation for the density and ionization energy of a many-particle system. *Phys. Rev. A* **1984**, *30*, 2745–2748.

(5) Kohn, W.; Sham, L. J. Self-consistent equations including exchange and correlation effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.

(6) Zhao, Q.; Morrison, R. C.; Parr, R. G. From electron densities to Kohn-Sham kinetic energies, orbital energies, exchange-correlation potentials, and exchange-correlation energies. *Phys. Rev. A* **1994**, *50*, 2138–2142.

(7) Vydrov, O. A.; Scuseria, G. E. Ionization potentials and electron affinities in the Perdew–Zunger self-interaction corrected density-functional theory. *J. Chem. Phys.* **2005**, *122*, 184107–184114.

(8) Adhikari, S.; Santra, B.; Ruan, S.; Bhattarai, P.; Nepal, N. K.; Jackson, K. A.; Ruzsinszky, A. The Fermi–Lo¨wdin self-interaction correction for ionization energies of organic molecules. *J. Chem. Phys.* **2020**, *153*, 184303–184313.

(9) Bi, S.; Carbogno, C.; Zhang, I. Y.; Scheffler, M. Self-interaction corrected SCAN functional for molecules and solids in the numeric atom-center orbital framework. *J. Chem. Phys.* **2024**, *160*, 034106 1–15.

(10) Ku¨mmel, S.; Kronik, L. Orbital-dependent density functionals: Theory and applications. *Rev. Mod. Phys.* **2008**, *80*, 3–60.

(11) Chong, D. P.; Gritsenko, O. V.; Baerends, E. J. Interpretation of the Kohn–Sham orbital energies as approximate vertical ionization potentials. *J. Chem. Phys.* **2002**, *116*, 1760–1772.

(12) Bartlett, R. J.; Lotrich, V. F.; Schweigert, I. V. Ab initio density functional theory: The best of both worlds? *J. Chem. Phys.* **2005**, *123*, 062205 1–21.

(13) Haiduke, R. L. A.; Bartlett, R. J. Communication: Can excitation energies be obtained from orbital energies in a correlated orbital theory? *J. Chem. Phys.* **2018**, *149*, 131101–131108.

(14) Powell, C. J. Recommended Auger parameters for 42 elemental solids. *J. Electron Spectros. Relat. Phenomena* **2012**, *185*, 1–3.

(15) Citrin, P. H.; Hamann, D. R. Measurement and calculation of polarization and

potential-energy effects on core-electron binding energies in solids: X-ray photoemission of rare gases implanted in noble metals. *Phys. Rev. B* **1974**, *10*, 4948–4963.

(16) Petersilka, M.; Gossmann, U.; Gross, E. Excitation energies from time-dependent density-functional theory. *Phys. Rev. Lett.* **1996**, *76*, 1212–1215.

(17) Shi, B.; Weissman, S.; Bruneval, F.; Kronik, L.; Og˘u¨t, S. Photoelectron spectra of¨ copper oxide cluster anions from first principles methods. *J. Chem. Phys.* **2018**, *149*, 064306–064312.

(18) Wang, L.-S.; Wu, H.; Desai, S. R.; Lou, L. Electronic structure of small copper oxide clusters: From Cu_2O to Cu_2O_4. *Phys. Rev. B* **1996**, *53*, 8028–8031.

(19) Wu, H.; Desai, S. R.; Wang, L.-S. Chemical Bonding between Cu and Oxygen Copper Oxides vs O2 Complexes: A Study of CuO x (x= 0- 6) Species by Anion Photoelectron Spectroscopy. *J. Phys. Chem. A* **1997**, *101*, 2103–2111.

(20) Krylov, A. I. Equation-of-motion coupled-cluster methods for open-shell and electronically excited species: The hitchhiker's guide to Fock space. *Annu. Rev. Phys. Chem.* **2008**, *59*, 433–462.

(21) Orms, N.; Krylov, A. I. Modeling photoelectron spectra of CuO, Cu2O, and CuO2 anions with equation-of-motion coupled-cluster methods: An adventure in Fock space. *J. Phys. Chem. A* **2017**, *122*, 3653–3664.

(22) Perdew, J. P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B* **1981**, *23*, 5048–5079.

(23) Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **1992**, *45*, 13244–13249.

(24) Pederson, M. R.; Ruzsinszky, A.; Perdew, J. P. Communication: Self-interaction correction with unitary invariance in density functional theory. *J. Chem. Phys.* **2014**, *140*, 121103 1–4.

(25) Zope, R. R.; Yamamoto, Y.; Diaz, C. M.; Baruah, T.; Peralta, J. E.; Jackson, K. A.; Santra, B.; Perdew, J. P. A step in the direction of resolving the paradox of PerdewZunger self-interaction correction. *J. Chem. Phys.* **2019**, *151*, 214108–214119.

(26) Akter, S.; Yamamoto, Y.; Diaz, C. M.; Jackson, K. A.; Zope, R. R.; Baruah, T. Study of self-interaction errors in density functional predictions of dipole polarizabilities and ionization energies of water clusters using Perdew–Zunger and locally scaled self-interaction corrected methods. *J. Chem. Phys.* **2020**, *153*, 164304 1–10.

(27) Skone, J. H.; Govoni, M.; Galli, G. Self-consistent hybrid functional for condensed systems. *Phys. Rev. B* **2014**, *89*, 195112 1–12.

(28) Ruzsinszky, A.; Perdew, J. P.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E. Spurious fractional charge on dissociated atoms: Pervasive and resilient self-interaction error of common density functionals. *J. Chem. Phys.* **2006**, *125*, 194112–194119.

(29) Cohen, A. J.; Mori-S´anchez, P.; Yang, W. Fractional charge perspective on the band gap in density-functional theory. *Phys. Rev. B* **2008**, *77*, 115123–115128.

(30) Porezag, D.; Pederson, M. R. Optimization of Gaussian basis sets for density-functional calculations. *Phys. Rev. A* **1999**, *60*, 2840–2848.

(31) Pederson, M. R.; Jackson, K. A. Variational mesh for quantum-mechanical simulations. *Phys. Rev. B* **1990**, *41*, 7453–7461.

(32) Pederson, M. R. Fermi orbital derivatives in self-interaction corrected density functional theory: Applications to closed shell atoms. *J. Chem. Phys.* **2015**, *142*, 1–6.

(33) Zope, R. R.; Baruah, T.; Yamamoto, Y.; Basurto, L.; Diaz, C. M.; Peralta, J. E.; Jackson, K. A. FLOSIC 0.2 based on the NRLMOL code of M. R. Pederson.

(34) Romero, S.; Yamamoto, Y.; Baruah, T.; Zope, R. R. Local self-interaction correction method with a simple scaling factor. *Phys. Chem. Chem. Phys.* **2021**, *23*, 2406–2418.

(35) Cherkes, I.; Klaiman, S.; Moiseyev, N. Spanning the Hilbert space with an even tempered Gaussian basis set. *Int. J. Quantum Chem.* **2009**, *109*, 2996–3002.

(36) Sun, Q. et al. Recent developments in the PySCF program package. *J. Chem. Phys.* **2020**, *153*, 024109–024129.

(37) Dunning Jr, T. H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(38) Kocheril, G. S.; Gao, H.-W.; Wang, L.-S. Observation of a long-lived triplet excited state and strong electron correlation effects in the copper oxide anion (CuO) using cryogenic photoelectron imaging. *J. Chem. Phys.* **2023**, *158*, 236101–136103.

(39) Bhattarai, P.; Santra, B.; Wagle, K.; Yamamoto, Y.; Zope, R. R.; Ruzsinszky, A.; Jackson, K. A.; Perdew, J. P. Exploring and enhancing the accuracy of interior-scaled Perdew–Zunger self-interaction correction. *J. Chem. Phys.* **2021**, *154*, 094105 1–11.

(40) Shahi, C.; Maniar, R.; Sah, R.; Peralta, J. E.; Jackson, K. A.; Perdew, J. P. A selfinteraction correction that does not throw out the baby with the bath water. in preparation.

(41) Chong, D. P. Computational study of the structures and photoelectron spectra of 12 azabenzenes. *Can. J. Chem.* **2019**, *97*, 697–703.

(42) Kanungo, B.; Kaplan, A. D.; Shahi, C.; Gavini, V.; Perdew, J. P. Unconventional error cancellation explains the success of Hartree–Fock density functional theory for barrier heights. *J. Phys. Chem. Lett.* **2024**, *15*, 323–328.

(43) Maniar, R.; Shukla, P. B.; Johnson, K., J; Jackson, K.; Perdew, J. P. Ionization energy: *s* – *d* transfer and SIC energy penalty in PZSIC. in preparation.

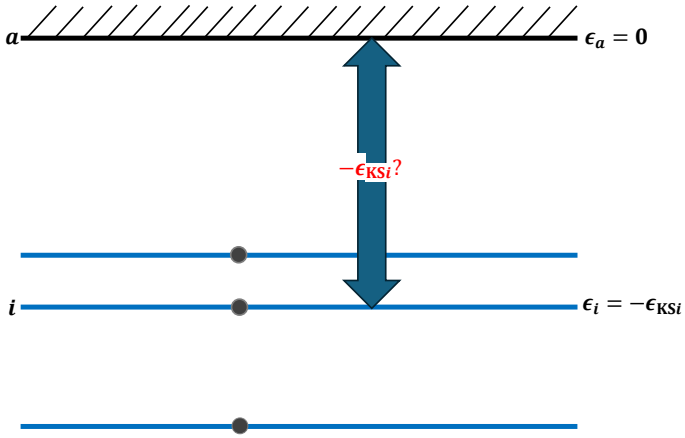
(44) Maniar, R.; Withanage, K. P. K.; Shahi, C.; Kaplan, A. D.; Perdew, J. P.; Pederson, M. R. Symmetry breaking and self-interaction correction in the chromium atom and dimer. *J. Chem. Phys.* **2024**, *160*, 144301 1–9.

(45) Casida, M. E. Time-dependent density functional response theory of molecular systems: theory, computational methods, and functionals. *Theor. Comput. Chem.* **1996**, *4*, 391–439.

(46) Appel, H.; Gross, E. K.; Burke, K. Excitations in time-dependent density-functional theory. *Phys. Rev. Lett.* **2003**, *90*, 043005 1–4.

(47) van Faassen, M.; Burke, K. Time-dependent density functional theory of high excitations: to infinity, and beyond. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4437–4450.

(48) Wasserman, A.; Maitra, N. T.; Burke, K. Accurate Rydberg excitations from the local density approximation. *Phys. Rev. Lett.* **2003**, *91*, 263001 1–5.


a
$\epsilon_a = 0$
$-\epsilon_{KSi}$?
i
$\epsilon_i = -\epsilon_{KSi}$