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When to trust photoelectron spectra from Kohn-Sham eigenvalues: The case of organic semiconductors

T. Körzdörfer and S. Kümmel
Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

N. Marom and L. Kronik
Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

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The combination of photoelectron spectroscopy and density functional theory is an important technique for clarifying a material's electronic structure. So far, however, it has been difficult to predict when the spectrum of occupied Kohn-Sham eigenvalues obtained from commonly used (semi-)local functionals bears physical relevance and when not. We demonstrate that a simple criterion based on evaluating each orbital's self-interaction allows prediction of the physical reliability of the eigenvalue spectrum. We further show that a self-interaction correction significantly improves the interpretability of eigenvalues also in difficult cases such as organic semiconductors where (semi-)local functionals fail.

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Photoelectron spectroscopy has emerged as one of the most important techniques for clarifying the electronic structure of molecules and solids. It plays a particularly important role in nanophysics and interface problems where other methods of determining a material's electronic structure are often hard to apply. Typically, such measurements are complemented by density functional theory (DFT)-based electronic structure calculations. The combination of experiment and theory then frequently allows to gain far-reaching physical insight, and this type of approach has been used very successfully in the past, as exemplified for finite systems by Refs. 1–7.

However, on the theoretical side this concept suffers from the fact that Kohn-Sham eigenvalues are frequently, but not always, good approximations to electron removal energies. Moreover, for some systems the eigenvalue spectrum changes a lot when going from one type of exchange-correlation potential (v_{xc}) to another. Important examples in this respect that are of great fundamental and practical interest are molecules used in organic electronics, e.g., Refs. 8–20. This limits the practical usefulness of interpreting Kohn-Sham eigenvalues because when discrepancies with experiment are observed, one does not know whether they are "real"[21] or just a reflection of the shortcomings of the employed density functional approximation.

Importantly, although Kohn-Sham eigenvalues are not exact quasiparticle excitation energies, the physical interpretation of Kohn-Sham eigenvalues does have a sound theoretical basis and is not coincidental. Interpreting the occupied eigenvalues is not to be confused with the notorious "band-gap problem,"[22] and it is a well-established fact that eigenvalues of energetically high-lying occupied orbitals, to which we restrict our analysis, are good approximations to electron removal energies when computed from a high-quality v_{xc}.[22–27] The pressing question is, then, when a practically used v_{xc} approximation leads to Kohn-Sham eigenvalues that can be trusted.

In this Rapid Communication we demonstrate that orbital self-interaction enters the structure of the occupied Kohn-Sham spectrum as a decisive factor. When different orbitals have significantly different spatial character, e.g., localized vs delocalized, their eigenvalues can carry largely different self-interaction errors (SIEs). In such cases the occupied Kohn-Sham eigenvalue spectrum no longer reflects the physical electron binding. We propose a simple test that does not predict the correct spectrum but can serve as a warning against possible misinterpretation of the occupied Kohn-Sham spectrum. We demonstrate that a parameter-free self-interaction correction (SIC) implemented rigorously within the Kohn-Sham framework[28] yields physically interpretable eigenvalues also in cases where (semi-)local approximations fail. Finally, we suggest a shortcut to approximately incorporate the effects of the SIC without the need to actually go through a SIC calculation.

Figure 1 exemplifies the typical problem that we have in mind. The bottom curve shows the experimental photoelectron spectrum of the 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecule,[9] which is a paradigm system in the field of organic semiconductors.[8] The top curve shows the occupied eigenvalues obtained from a local density approximation (LDA) calculation in the typically used density-of-states (DOS) interpretation: the eigenvalues are convoluted with a Gaussian and shifted to compensate for the wrong intrinsic asymptotics of the LDA potential.[2,4] For ease of comparison we align all spectra in this Rapid Communication such that the highest-occupied molecular orbital (HOMO) energies match. Although this type of procedure leads to very good agreement with experiment for many systems it fails badly for PTCDA. The second peak of the LDA spectrum is right where the experimental spectrum shows a pronounced gap between the HOMO and the HOMO-1 peak. Using a generalized gradient approximation (GGA) functional hardly changes the picture. This is disconcerting because this part of the spectrum is weakly bound and effects that make the eigenvalue interpretation doubtful for energetically deep lying states[27] are unimportant. It is also puzzling from the perspective that the geometry of PTCDA is well described by (semi-)local functionals, which could lead one to expect an overall correct description.

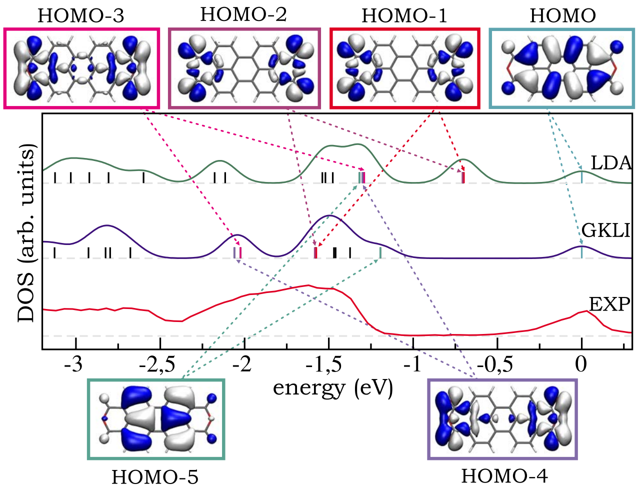

FIG. 1. (Color online) Simulated and measured photoemission spectra of PTCDA. From top to bottom: isosurface plots of Kohn-Sham orbitals (labels HOMO, HOMO-1, etc., refer to the LDA ordering), Kohn-Sham eigenvalues broadened by 0.1 eV for LDA and GKLI, and gas phase experimental data from Ref. 9. Note that the experiment shows a pronounced gap between the HOMO and the HOMO-1 peaks that is reproduced by the GKLI spectrum but not by the LDA one.

By employing the *GW* method or by resorting to hybrid functionals that incorporate empirical parameters, one can obtain a theoretical spectrum that does reproduce the experimental HOMO-HOMO-1 gap[9] but at the price of a tremendously increased computational effort or at the price of an increased computational effort *and* additional parameters that may hinder performance for other systems,[29] respectively. Therefore, from a practical point of view it would be extremely helpful to (i) have a criterion that signals whether the approximative interpretation of the Kohn-Sham eigenvalues is justified for a given system and v_{xc} approximation and (ii) have a method to obtain physically reliable eigenvalues in cases where approximations such as LDA and GGAs fail. Both are presented below.

The desired *a priori* knowledge about the reliability of the Kohn-Sham eigenvalue spectrum, e.g., as obtained with LDA, can be gained simply by evaluating each orbital's SIE,

$$e_i = \langle \varphi_i | v_H[|\varphi_i|^2] | \varphi_i \rangle + \langle \varphi_i | v_{\mathrm{xc}}[|\varphi_i|^2, 0] | \varphi_i \rangle. \qquad (1)$$

Here, $v_{\mathrm{xc}}[|\varphi_i|^2, 0]$ denotes the approximate expression for the (spin-polarized) exchange-correlation potential, in our case LDA, evaluated with the corresponding Kohn-Sham orbital density $|\varphi_i|^2$. v_H is the corresponding Hartree potential. Equation (1) is the change one expects in the ith eigenvalue from first-order perturbation theory when one applies a self-interaction correction.[30]

Self-interaction is one of the most prominent problems in present-day DFT (Ref. 22) and was identified as a fundamental difficulty early on.[30] For the unknown exact exchange-correlation energy functional, the SIE defined in Eq. (1) must vanish when the potentials are evaluated on a one-electron density.[28,30] Since every Kohn-Sham orbital density has the structure of a one-electron density, Eq. (1) should vanish in exact DFT. However, it is nonzero when an approximation such as LDA or GGA is employed. Thus, every Kohn-Sham orbital's eigenvalue will be offset to some extent due to orbital self-interaction. In terms of a photoelectron interpretation this need not be a problem if all orbitals suffer from roughly the same amount of SIE because then all occupied eigenvalues will be offset by roughly the same value and the structure of the spectrum will be preserved. However, if a system consists of orbitals, wherein some carry large self-interaction and others little, then the SIE will distort the spectrum and it will no longer reflect the physical nature of the electronic binding.

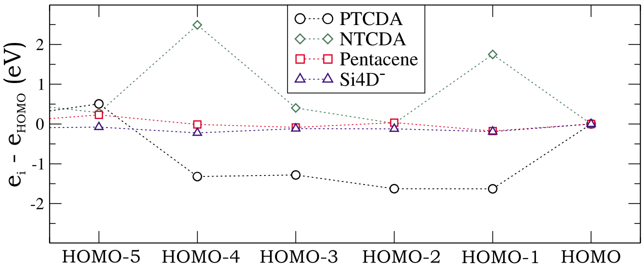

FIG. 2. (Color online) Orbital self-interaction e_i for the least bound LDA orbitals of PTCDA, NTCDA, pentacene, and $\mathrm{Si_4D^-}$ relative to the respective e_{HOMO}. Dashed lines are a guide to the eye.

That orbital self-interaction is indeed a reason for the disagreement seen for PTCDA becomes clear from Fig. 2. It shows e_i-e_{HOMO}, i.e., the self-interaction error of each orbital relative to the one of the system's HOMO, evaluated for the highest LDA Kohn-Sham orbitals for four different systems. This relative error is the quantity relevant for the usual comparison to experiment in which the HOMO peaks are aligned. First focusing on the black circles denoting the results for PTCDA, it is evident that the orbitals from HOMO-1 to HOMO-4 carry much larger self-interaction than, e.g., HOMO and HOMO-5. Figure 1 depicts these orbitals and indicates which peak in the DOS interpretation is associated with them. HOMO-1 and HOMO-2 are the orbitals whose eigenvalues lie where the experiment shows a pronounced gap in the spectrum.

In order to check whether this finding is coincidental or systematic we have repeated the analysis for other systems. With $\mathrm{Si_4D^-}$ and pentacene we have chosen two very different systems—but for both it is known that the eigenvalues from (semi-)local functionals can quite reasonably be compared to experiment.[4,16,31] Figure 2 reveals that this is in agreement with the e_i analysis: for both systems (and for other clusters that are not shown here and for which LDA also yields a reasonable DOS), all of the high-lying orbitals carry very similar SIE. Thus, we note as a first important result that Eq. (1) can be used to warn against possible misinterpretation of occupied Kohn-Sham eigenvalues.

One may wonder why e_i varies strongly over the orbitals for some systems and hardly varies for others. In a nutshell, the answer is that in systems in which the high-lying occupied orbitals all have a similar spatial structure, they typically also carry similar self-interaction. Returning to the example of PTCDA depicted in Fig. 1 we see that here different

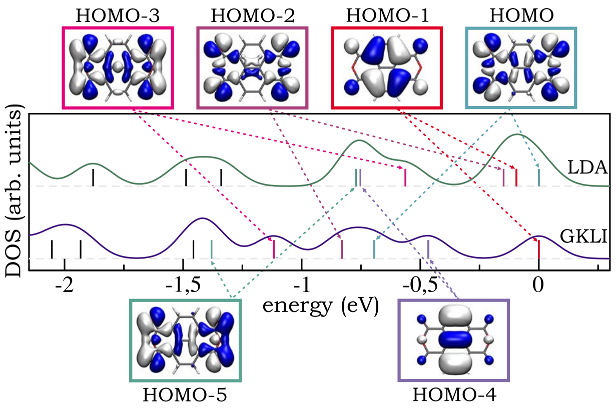

FIG. 3. (Color online) DOS plots for NTCDA from occupied Kohn-Sham eigenvalues as obtained in LDA and GKLI, and isosurface plots of Kohn-Sham orbitals as in Fig. 1. Again, GKLI opens a gap between HOMO and HOMO-1 that is not seen with the LDA.

orbitals have a rather different spatial structure: HOMO and HOMO-5 lead to probability densities that are delocalized over the entire molecule, whereas the other shown orbitals correspond to densities on the anhydride (side) groups. Thus, the observation of largely different e_i can be rationalized by the fact that self-interaction is related to localization.[30,32]

With self-interaction thus identified as a main source of error, the following question arises: what should one do once one has realized through the above analysis that orbital self-interaction is likely to distort the occupied Kohn-Sham spectrum for the system of interest? In view of the above findings it is a natural idea to resort to a density functional which reduces self-interaction. A first-principles parameter-free approach to achieve this is the SIC.[30] It can rigorously be brought under the umbrella of Kohn-Sham theory in the generalized optimized effective potential (GOEP) approach,[28] which includes energy-minimizing orbital transformations in the self-consistent iteration. Therefore, the Krieger-Li-Iafrate (KLI) approximation made to the GOEP (called GKLI) is reliable, whereas the KLI approximation made to the usual optimized effective potential (OEP) equation for the SIC is not.[33] As the SIC approach does include correlation and only requires evaluation of the self-exchange integrals, it is an attractive alternative to pure exact exchange or hybrid functional methods. The middle part of Fig. 1 shows the spectrum of occupied Kohn-Sham eigenvalues obtained using the GKLI approach. As one can see from the relation between the orbitals and their corresponding eigenvalues, the GKLI spectrum corrects the failure of LDA, opening a gap between HOMO and HOMO-1 that corresponds well to the experimentally observed gap.

The data shown in Figs. 2 and 3 for 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) confirm that the relation between orbital structure and eigenvalue correction is not coincidental. Similar to PTCDA there are orbitals of different spatial structure, and again, switching from LDA to GKLI opens a gap between HOMO and HOMO-1. We also verified that the SIC has practically no effect on the spectrum of pentacene and Si_4D^-. Thus, we have arrived at a second important result: A self-interaction free approach can yield physically interpretable occupied eigenvalues also in cases where (semi-)local functionals fail.

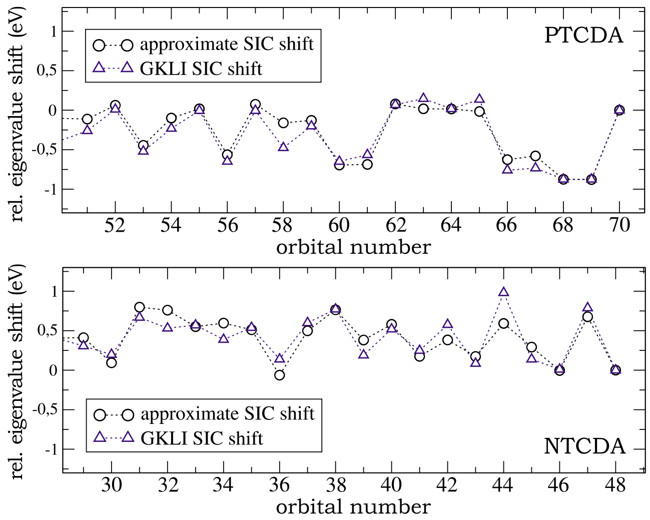

FIG. 4. (Color online) Orbital shift relative to the shift for the HOMO as obtained from the GKLI calculation (blue triangles) and Eq. (2) (black circles) for PTCDA (top) and NTCDA (bottom). The HOMO is orbital number 70 (top) or 48 (bottom), respectively.

Finally, the results so far beg an obvious question: having realized that the problem of physically meaningful eigenvalues is closely related to SIE and orbital structure, can one estimate the effect that the SIC will have on the occupied eigenvalues without actually having to go through a full SIC calculation? The answer is yes. Estimating the Hartree and LDA exchange contributions while neglecting the difference between SI-corrected and uncorrected orbitals as in Refs. 30 and 34, but additionally taking into account LDA correlation, one can estimate (using atomic units) the self-interaction corrected eigenvalue purely from LDA quantities by

$$\varepsilon_i^{\mathrm{est}} = \varepsilon_i^{\mathrm{LDA}} - 0.94\int (|\varphi_i|^2)^{4/3} d^3r - \langle \varphi_i | v_c^{\mathrm{LDA}}[|\varphi_i|^2, 0] | \varphi_i \rangle . \tag{2}$$

Figure 4 compares the shift of the GKLI eigenvalues relative to the GKLI shift for the HOMO, i.e., $(\varepsilon_i^{\mathrm{GKLI}} - \varepsilon_i^{\mathrm{LDA}}) - (\varepsilon_{\mathrm{HOMO}}^{\mathrm{GKLI}} - \varepsilon_{\mathrm{HOMO}}^{\mathrm{LDA}})$ to the same relative shift evaluated with the estimated eigenvalues, i.e., $(\varepsilon_i^{\mathrm{est}} - \varepsilon_i^{\mathrm{LDA}}) - (\varepsilon_{\mathrm{HOMO}}^{\mathrm{est}} - \varepsilon_{\mathrm{HOMO}}^{\mathrm{LDA}})$. Again, this relative shift is the quantity relevant for the usual comparison to experiment. In view of the simplicity of Eq. (2) which can be evaluated straightforwardly based on the ingredients of a standard LDA code, the approximation works well. Thus, our third result is that via Eq. (2) one can obtain an estimate of the effects that SIC will have on the occupied eigenvalues with very little computational effort.

In summary, we have shown that orbital self-interaction is decisive for the interpretability of the occupied Kohn-Sham spectrum as a DOS as measured in photoelectron spectroscopy. It can serve as a transparent criterion to judge the interpretability of the occupied Kohn-Sham spectrum. A self-interaction correction implemented within the Kohn-Sham framework can yield reliable spectra also in such cases where (semi-)local density functionals fail, and its effect on the eigenvalues can be estimated with little effort. These findings extend the range of systems for which reliable predictions can be made, as demonstrated here for prototypical organic semiconductor molecules.

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[1] N. Binggeli and J. R. Chelikowsky, Phys. Rev. Lett. **75**, 493 (1995); J. Muller, B. Liu, A. A. Shvartsburg, S. Ogut, J. R. Chelikowsky, K. W. Michael Siu, K. M. Ho, and G. Gantefor, *ibid.* **85**, 1666 (2000).

[2] J. Akola, M. Manninen, H. Häkkinen, U. Landman, X. Li, and L.-S. Wang, Phys. Rev. B **62**, 13216 (2000).

[3] S. N. Khanna, M. Beltran, and P. Jena, Phys. Rev. B **64**, 235419 (2001).

[4] L. Kronik *et al.*, Nature Mater. **1**, 49 (2002); Eur. Phys. J. D **24**, 33 (2003).

[5] N. Bertram, Y. D. Kim, G. Ganteför, Q. Sun, P. Jena, J. Tamuliene, and G. Seifert, Chem. Phys. Lett. **396**, 341 (2004).

[6] H. Häkkinen, M. Moseler, O. Kostko, N. Morgner, M. A. Hoffmann, and B. v. Issendorff, Phys. Rev. Lett. **93**, 093401 (2004).

[7] G. Tu, V. Carravetta, O. Vahtras, and H. Agren, J. Chem. Phys. **127**, 174110 (2007).

[8] E. Umbach and R. Fink, in *Proceedings of the International School of Physics "Enrico Fermi*," edited by V. M. Agrenovich and G. C. La Rocca (IOS Press, Amsterdam, 2002), p. 233.

[9] N. Dori, M. Menon, L. Kilian, M. Sokolowski, L. Kronik, and E. Umbach, Phys. Rev. B **73**, 195208 (2006).

[10] G. Heimel, L. Romaner, J.-L. Brédas, and E. Zojer, Surf. Sci. **600**, 4548 (2006).

[11] N. Marom, O. Hod, G. E. Scuseria, and L. Kronik, J. Chem. Phys. **128**, 164107 (2008); N. Marom, O. Hod, G. E. Scuseria, and L. Kronik, Appl. Phys. A **95**, 159 (2009); **95**, 165 (2009).

[12] C. Risko, C. D. Zangmeister, Y. Yao, T. J. Marks, J. M. Tour, M. A. Ratner, and R. D. van Zee, J. Phys. Chem. C **112**, 13215 (2008).

[13] S. Yanagisawa and Y. Morikawa, Chem. Phys. Lett. **420**, 523 (2006).

[14] M. Rohlfing, R. Temirov, and F. S. Tautz, Phys. Rev. B **76**, 115421 (2007).

[15] M. L. Tiago, J. E. Northrup, and S. G. Louie, Phys. Rev. B **67**, 115212 (2003).

[16] K. Hummer and C. Ambrosch-Draxl, Phys. Rev. B **72**, 205205 (2005).

[17] S. Kera, H. Yamane, H. Fukagawa, T. Hanatani, K. K. Okudaira, K. Seki, and N. Ueno, J. Electron Spectrosc. Relat. Phenom. **156-158**, 135 (2007).

[18] X. Zhan, C. Risko, F. Amy, C. Chan, W. Zhao, S. Barlow, A. Kahn, J.-L. Brédas, and S. R. Marder, J. Am. Chem. Soc. **127**, 9021 (2005).

[19] H. Vázquez, R. Oszwaldowski, P. Pou, J. Ortega, R. Pérez, F. Flores, and A. Kahn, Europhys. Lett. **65**, 802 (2004).

[20] S. Duhm, G. Heimel, I. Salzmann, H. Glowatzki, R. L. Johnson, A. Vollmer, J. P. Rabe, and N. Koch, Nature Mater. **7**, 326 (2008).

[21] "Real" differences may arise from systematic deviations between Kohn-Sham eigenvalues and quasiparticle excitation energies, e.g., for deep lying (Ref. 27) or strongly coupled excitations (Ref. 35), from matrix element effects, or other experimental intricacies.

[22] S. Kümmel and L. Kronik, Rev. Mod. Phys. **80**, 3 (2008).

[23] J. F. Janak, Phys. Rev. B **18**, 7165 (1978).

[24] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984); C.-O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).

[25] A. Görling, Phys. Rev. A **54**, 3912 (1996).

[26] C. Filippi, C. J. Umrigar, and X. Gonze, J. Chem. Phys. **107**, 9994 (1997).

[27] D. P. Chong, O. V. Gritsenko, and E. J. Baerends, J. Chem. Phys. **116**, 1760 (2002).

[28] T. Körzdörfer, S. Kümmel, and M. Mundt, J. Chem. Phys. **129**, 014110 (2008). Computational details of our approach can be found in this paper.

[29] J. Paier, M. Marsman, and G. Kresse, J. Chem. Phys. **127**, 024103 (2007).

[30] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[31] H. Fukagawa, H. Yamane, T. Kataoka, S. Kera, M. Nakamura, K. Kudo, and N. Ueno, Phys. Rev. B **73**, 245310 (2006); O. McDonald *et al.*, Surf. Sci. **600**, 3217 (2006); M. L. M. Rocco *et al.*, J. Chem. Phys. **129**, 074702 (2008).

[32] A study quantifying the amount of localization and its relation to e_i will be presented elsewhere.

[33] T. Körzdörfer, M. Mundt, and S. Kümmel, Phys. Rev. Lett. **100**, 133004 (2008).

[34] R. S. Gadre, L. J. Bartolotti, and N. C. Handy, J. Chem. Phys. **72**, 1034 (1980).

[35] M. Mundt and S. Kümmel, Phys. Rev. B **76**, 035413 (2007); M. Walter and H. Häkkinnen, New J. Phys. **10**, 043018 (2008).