Koopmans’ springs to life

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The meaning of orbital energies (OOEs) in Kohn–Sham (KS) density functional theory (DFT) is subject to a longstanding controversy. In local, semilocal, and hybrid density functionals (DFs) a Koopmans’ approach, where OOE approximate negative ionization potentials (IPs), is unreliable. We discuss a methodology based on the Baer–Neuhauser–Livshits range-separated hybrid DFs for which Koopmans’ approach “springs to life.” The OOE are remarkably close to the negative IPs with typical deviations of ∓0.3 eV down to IPs of 30 eV, as demonstrated on several molecules. An essential component is the ab initio motivated range-parameter tuning procedure, forcing the highest OOE to be exactly equal to the negative first IP. We develop a theory for the curvature of the energy as a function of fractional occupation numbers to explain some of the results. © 2009 American Institute of Physics. [doi:10.1063/1.3269030]

An attractive feature of the Hartree–Fock (HF) theory is the interpretation inspired by Koopmans’1 that negative occupied orbital energies (OOEs) approximate ionization potentials (IPs) of atoms and molecules. Whether this is true in density functional theory (DFT) is subject to a longstanding controversy.2–11 It has been established that the negative energy of the highest occupied molecular orbital (HOMO) in the Kohn–Sham (KS) DFT is equal to the first IP.5,14 This holds also for generalized Kohn–Sham (GKS) approaches.15,16 As for the meaning of the deeper KS OOEs, opinions vary: From “there is no physical meaning at all”3 to “exact KS negative OOEs are close to IPs even for low-lying energy levels.”9

Numerical and theoretical evidences demonstrate that exact KS OOEs are excellent approximations to quasiparticle energies obtained by Green’s function methods.17–20 This sharply contrasts the failure of local/semilocal and hybrid DFs. The specific RSH we use combines the Baer–Neuhauser–Livshits range-separated hybrid DFs for occupied molecular orbital (HOMO = IP) and a local/semilocal short-range approximation of the time-dependent GKS equations’ cation excitation energies.44,45 We test how calculated IPs compare to experimental IPs and how the two methods compare to each other. To avoid basis-set truncation errors we used Dunning’s correlation-consistent polarized valence-quadruple-zeta (CC-PVQZ) basis-sets throughout. Geometries of N2, O2, F2, water (H2O), ammonia (NH3), formaldehyde (CH2O), and formic acid (HCOOH) were optimized with the coupled-cluster singles doubles (CCSD) method, with the HF method, with KS–DFT at the local spin-density approximation (LSDA) level, with the gradient corrected BP86 (Becke exchange and Perdew’s 86 correlation DF), with Becke’s hybrid, B3LYP, with B3P86 and the B3P86−30% hybrid and with BNL. In the latter, γ was adjusted for each neutral system to reproduce \( -\epsilon_{\text{HOMO}} = IP_{\text{ASCF}} \). Coupled cluster IPs were calculated as single points with disconnected triples [CCSD(T)] on the CCSD geometries. BNL calculations used QCHEM 3.2.48 Other DF calculations used GAUSSIAN 03.49 We used the random-phase approximation option for the time-dependent

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DFT (TDDFT) calculations, except for $F_2$ and $O_2$, where only Tamm–Dancoff option converged.

In Fig. 1 we compare several estimates with experimental vertical IPs for $H_2O$, $NH_3$, $HCOOH$, $CH_2O$, $N_2$, and $F_2$. More detailed data are given in the supporting information. The $F_2$ results deserve special attention, as the cation ground excited state is doubly degenerate where the hole can be in $g^+$ or $g^-$ or in $u^+$ or $u^−$ orbitals. Thus, there are two types of hole transitions: $g^+ \rightarrow u^+$ or $g^+ \rightarrow u^−$ which have the same energy but TDDFT breaks this degeneracy due to functional deficiency. The TD data for $IP_2$ of $F_2$ in Fig. 1 refers to the $\pi^+ \rightarrow \pi^+$ transition. We summarize the results in Fig. 1:

1. HF theory deviances vary in the range −2 and 2 eV for all systems. Koopmans’ deviances are positive while $\Delta$SCF/TD IPs are usually negative. For $N_2^+$, HF spuriously predicts $\Pi_u$ ground state symmetry instead of $\Sigma_g^−$. For $F_2$, HF predicts $\Sigma_u^+$ symmetry for the first excited cation state instead of $\Pi_u$. KS and GKS methods avoid such large qualitative errors.
2. LSDA: Koopmans’ deviances are large (−5 to −8 eV) and non-uniform because SR is larger in localized

FIG. 1. Deviance of negative OOE's and SCF/TD energies relative to vertical IPs derived from experiment data (Refs. 50–52) for several molecules. KS and SAOP OOE's data are taken from Ref. 9.
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tals.\textsuperscript{12} $\Delta$SCF/TD deviances are about 1 eV.

(3) B3LYP: Koopmans’ deviances are still large, $-3$ to $-4$ eV, but more uniform than in LSDA due to smaller SR. $\Delta$SCF/TD IPs deviances are small (0.5 eV).

(4) BNL*: IPs, whether computed by Koopmans’ or $\Delta$SCF/TD methods, exhibit low deviances. For the larger molecules the deviances are 0.3 eV or less while for diatomics some OOE s have larger deviances (note: the $N_2$ experimental $I_P$ is insecure and the peak is multiconfigurational\textsuperscript{13}). BNL* deviations are small even for deep valence orbitals (IPs of $-20$ to $-33$ eV). BNL* OOE s are also close to true KS OOE s and slightly superior to statistical averaging of orbital potentials (SAOP) results.\textsuperscript{9} The performance for $\sigma$-orbitals is better than for $\pi$-orbitals. BNL* Koopmans’ and $\Delta$SCF/TD IPs are close for both outer and inner orbitals. For core orbitals of water and $N_2$ BNL OOE s are 5 and 8 eV higher than true KS orbitals, $-25$ eV above experimental IPs.\textsuperscript{9}

(5) In LSDA, B3LYP, and BNL the SCF/TD predictions for the IPs are all reasonably good in accordance with previously established results (provided the states do not have double excitation character).

One can improve the LSDA and B3LYP Koopmans’ IP predictions by adding a constant shift $I_P(\Delta$SCF$)+\varepsilon_f$. This works better for B3LYP than for LSDA (because of SR): the IP deviances of the first three orbital energies in $H_2O$ are fairly constant in LSDA/B3LYP, $-4$ eV to $-5$ eV, but that of the compressed 2a1 orbital, deviates by 2 eV in LSDA and by 0.6 eV in B3LYP. In BNL* this effect is unnoticeable.

We now provide a theory to help explain some of the numerical results. Following Refs. 22 and 54 we highlight the concept of the curvature of the energy $E_{gs}$ (in KS/ GKS/HF theories) with respect to $f_i$, the occupation number of the $i$th molecular orbital $\psi_i(r)$. The importance of curvature stems from Janak’s theorem\textsuperscript{25} $\varepsilon_i=\partial E_{gs}/\partial f_i$, so:

$$E_{gs}[N-1;i]-E_{gs}[N]=\int_1^0 \varepsilon_i(f_i)df_i,$$

where $E_{gs}[N]$ is the ground state energy of the $N=2N_H$ closed shell electron system ($N_H$ is the index of the HOMO) and $E_{gs}[N-1;i]$ is the hole-constrained DFT ground state of the $N-1$ electron system with a hole at the $i$th orbital. This “fully relaxed” excited state energy for the cation approximates the variational excited state DFT method,\textsuperscript{56} so the left hand side of Eq. (1) approximates $IP_{N_{gs}[i]}-i$. When the curvature ($\partial^2 E_{gs}/\partial f_i^2=\partial \varepsilon_i/\partial f_i$) is zero, as it is for the HOMO in exact KS or GKS theories, then the right-hand side of Eq. (1) equals $-\varepsilon_i$ and this is approximately equal to the relevant $IP_{N_{gs}[i]}-i$. When the curvature is positive, Eq. (1) yields $-\varepsilon_i(1)<IP_{N_{gs}[i]}-i$, as found in calculations with approximate DFs for the HOMO energy, discussed in Refs. 22 and 54.

We now give an expression for the full curvature matrix: $C_{mi}=\langle \partial^2 E_{gs}/\partial f_m \partial f_i \rangle=\langle \partial \varepsilon_i/\partial f_m \partial f_i \rangle$. For clarity, we assume closed shell molecules and we suppress the spin design- nation for the orbitals $\psi_i(r)$ and OOE s. The Hamiltonian $\hat{H}$ is given by $\partial^2 E_{gs}/(\partial \psi_i(r))=\hat{H}\psi_i(r)$ and the density matrix is $\Sigma_f \psi_i(r)\psi_i(r')$. The KS/GKS equations assert that $\hat{H}\psi_i=\varepsilon_i \psi_i$ and since $f_i$ are parameters in $\hat{H}$, we have\textsuperscript{57}

$$\delta \psi_i(r)/\delta f_i=\Sigma_f \psi_i \omega_{jk} A_{jk} \psi_j(r),$$

where $A_{jk}(\psi)=\langle \psi_j| \partial \hat{H}/\partial f_i |\psi_k \rangle$ and $\omega_{ij}=\varepsilon_i-\varepsilon_j$ in particular $C_{mi}=A_{mn}(\varepsilon_i)$. Now, $\partial^2 \varepsilon_i/\partial f_i$ not only creates the matrix elements $A_{jk}(\varepsilon_i)$ but also depends on them and from this,

$$A_{mn}(\varepsilon_i)=\sum_{jk} (\varepsilon_j-\varepsilon_k) W_{jk}(\varepsilon_i),$$

where the $W$ matrix corresponds to linear response kernel,

$$W_{jk}(\varepsilon_i)=\int d^3 r f_XC(r)\left(\frac{1}{r-r'}+f_XC(r-r')\right) \psi_j(r) \psi_k(r').$$

This matrix arises from the dependency of the molecular orbitals on the occupation numbers. $R^{-1}$ is the inverse of the total response matrix,

$$R_{jk}(\varepsilon_i)=\delta_{jk}(\varepsilon_i)+\omega_{im}(f_n-f_m)W_{jk}(\varepsilon_i).$$

In Eq. (3), $f_XC(r)\psi_j(r')=\delta_XC[n(r)]/\delta(r')$ is the XC kernel and $v_{XC}[n(r)]$ is the KS or GKS XC potential. In HF theory $f_XC$ is zero. The function $u(r)$, describing orbital exchange, is zero in KS theory, $1/r$ in the HF theory, and its choice characterizes the kind of GKS theory used: $u(r)=\lambda/r$ (where $0<\lambda<1$) for hybrid DFs (in B3LYP $\lambda=0.2$) and $u(r)=\text{crf}(\gamma r)/r$ for RSH (BNL) DFs (in this latter case $v_{XC}[n(r)]$ is dependent on the range-parameter $\gamma$ as well).

The relation in Eq. (2) is exact but difficult to analyze. To simplify, we neglect the off-diagonal elements of the matrix $R$ in Eq. (4), neglecting all $W_{mm}(\varepsilon_i)$ in Eq. (4) except for same-pair interactions, when $(mn)=(ij)$. In this case $A_{mn}(\varepsilon_i)=W_{mn}(\varepsilon_i)/R_{mn}(\varepsilon_i)$ and in particular,

$$C_{mi}=A_{mn}(\varepsilon_i)=W_{mn}(\varepsilon_i).$$

Applying this result to orbital $\varepsilon_i$ itself we find the curvature element $C_{ii}=W_{ii}(\varepsilon_i)$, i.e.,

$$C_{ii}=\int d^3 r f_XC(r)\left(\frac{1}{r-r'}+f_XC(r-r')\right) \psi_i(r) \psi_i(r'),$$

where $u(r)=r^{-1}-u(r)$. For the HF theory both $f_XC$ and $u(r)$ vanish and thus $C_{ii}=0$, a result corroborated for $i=N_H$ in calculations, showing small curvature, only slightly negative.\textsuperscript{31,54,58,59} For local/semilocal hybrid DFs, $u(r)=(1-\lambda)/r$ ($\lambda=0$, local/semilocal and $\lambda=0.2$, B3LYP) and $f_XC(r)\psi_j(r')=\delta_XC[r-r']$, leading to $W_{ii}(\varepsilon_i)$ dominated by positive Hartree SR energy for orbital $\psi_i(r)$. This gives significant positive curvature, within semilocal DFs as corroborated by numerical calculations.\textsuperscript{31,54,58–60} We are not aware of calculations for hybrids. Positive curvature grows for localized orbitals as these have large SR. Thus LSDA IPs have larger deviances than B3LYP, which has partial cancellation of SR. In the exact KS theory, the nonlocal $f_XC(r)\psi_j(r')$ kernel cancels SR and the curvature should be small. In GKS-RSH theories,
which are intermediate between HF and local KS theories, self-interaction is small and the rule that $C_{ii} = 0$ holds well as seen in numerical calculations. In BNL curvatures are small but not exactly zero, thus requiring $\gamma$-tuning to have the initial slope $\delta E_{gs}/\delta f|_{\gamma=1}$ equal to the average slope $-P_{1} = E_{gs}[N] - E_{gs}[N-1]$.

Summarizing, we gave numerical and theoretical evidence suggesting that $ab$ initio motivated $\gamma$-tuned BNL enables that of Koopmans’ approach using OOE to approximate IPs to good accuracy. The tuning procedure was found essential for quantitative predictions in other “tough” problems for DFT and TDDFT.

Supplemental material is available.

Table with IPs for $N_2$, $O_2$, $F_2$, $H_2O$, $NH_3$, $CH_2O$, and $HCOOH$ at various theoretical levels.

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