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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 OOEs 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 OOEs are remarkably close to the negative IPs with typical deviances 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.[2–13] 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.[6,14] 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: HOMO energies underestimate first IPs by several electron volts.[21,22] As demonstrated below, this holds for deeper OOEs as well.[4,5] One problem of approximate DFs is the presence of spurious self-interaction[14,23] [mostly exchange not canceling Hartree self-repulsion (SR)[2]] artificially increasing OOEs of localized orbitals.[12] Mitigating self-interaction[2,24–31] can be achieved with range-separated hybrids (RSHs), applied within a GKS formalism.[21,32–41] In RSHs, the exchange energy splits into two: an explicit long-range orbital $(\mathrm{erf}(\gamma r)/r)$ and a local/semilocal short-range $(\mathrm{erfc}(\gamma r)/r)$ components. γ is the range-parameter (in a_0^{-1}).

In this letter, we discuss the use RSHs for estimating of IPs. The specific RSH we use combines the Baer–Neuhauser–Livshits (BNL) RSH DF[21] and the *ab initio* motivated range-parameter tuning procedure (γ-tuning, where γ is the range-parameter). Our tuning procedure enforces the exact GKS condition $-\varepsilon_{\mathrm{HOMO}} = \mathrm{IP}_{\Delta \mathrm{SCF}}$ (Refs. 16 and 21) as-

sociating quantities from differing charge states of the system. Such procedure is implemented as a line search and was discussed in Ref. 21, requiring few additional self-consistent field (SCF) ground state calculations of the neutral and its cation. We present the IP predictions and compare to standard DFs. Range-parameter tuning procedures ameliorate several prominent failures of common DFT applications: dissociation of radicals,[42,43] localization of charge in weakly interacting systems,[44] charge-transfer excitations,[45] and band gaps in solids.[46] Finally, we develop a theory that partially explains the success of tuned RSHs and the failures of local, semilocal, and hybrid DFs.

We first compare IPs calculated using traditional DFs and tuned-γ BNL (BNL*) for small molecules. We check two ways for estimating IPs: (1) "Koopmans':" set $\mathrm{IP}_k = -\varepsilon_{N_e-k+1}$. (2) "$\Delta$SCF/TD:" the first IP ($\mathrm{IP}_1$) is estimated using a ΔSCF procedure (the cation neutral SCF energy difference) and $\mathrm{IP}_{k+1} = \mathrm{IP}_1 + h\nu_k$ $(k=1,2,\ldots)$, where $h\nu_k$ are the time-dependent GKS equations' cation excitation energies. 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[47] throughout. Geometries of N_2, O_2, F_2, water (H_2O), ammonia (NH_3), formaldehyde (CH_2O), 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 $-\varepsilon_{\mathrm{HOMO}} = \mathrm{IP}_{\Delta \mathrm{SCF}}$. 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

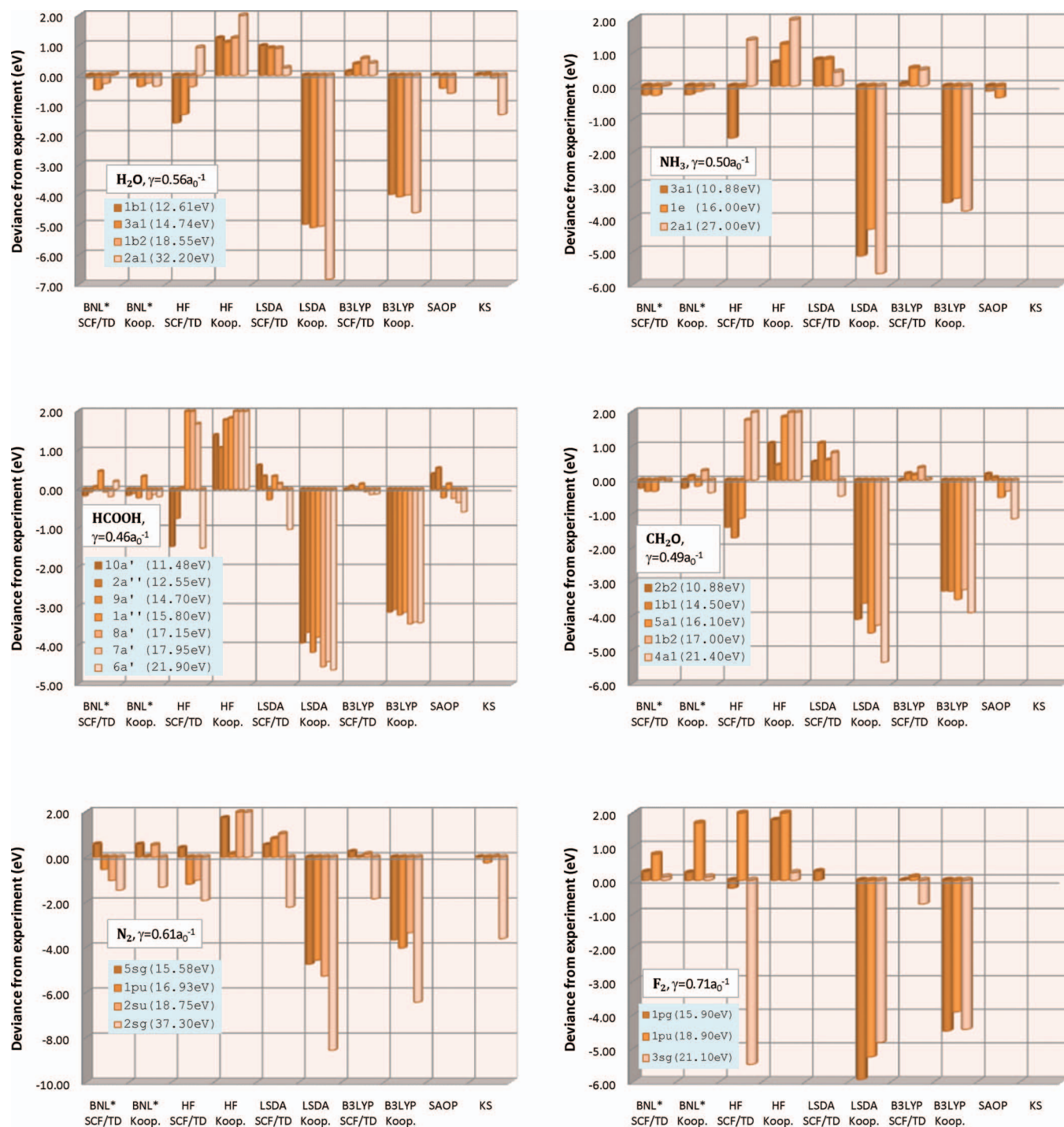a)Electronic mail: salzner@fen.bilkent.edu.tr.
b)Electronic mail: roi.baer@huji.ac.il.

FIG. 1. Deviance of negative OOEs and SCF/TD energies relative to vertical IPs derived from experiment data (Refs. 50–52) for several molecules. KS and SAOP OOEs data are taken from Ref. 9.

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 π_g^+ or in π_g^- (π_u^+ or in π_u^-) orbitals. Thus, there are two types of hole transitions: $\pi_g^+ \rightarrow \pi_u^+$ or $\pi_g^+ \rightarrow \pi_u^-$ 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

$\pi_g^+ \rightarrow \pi_u^+$ 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 ΔSCF/TD IPs are usually negative. For N_2^+, HF spuriously predicts Π_u ground state symmetry instead of Σ_g. For F_2, HF predicts Σ_g symmetry for the first excited cation state instead of Π_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

orbitals.[12] ΔSCF/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. ΔSCF/TD IPs deviances are small (0.5 eV).

(4) BNL*: IPs, whether computed by Koopmans' or ΔSCF/TD methods, exhibit low deviances. For the larger molecules the deviances are 0.3 eV or less while for diatomics some OOEs have larger deviances (note: the N_2 experimental IP$_4$ is insecure and the peak is multiconfigurational[53]). BNL* deviances are small even for deep valence orbitals (IPs of -20 to -33 eV). BNL* OOEs are also close to true KS OOEs and slightly superior to statistical averaging of orbital potentials (SAOP) results.[9] The performance for σ-orbitals is better than for π-orbitals. BNL* Koopmans' and ΔSCF/TD IPs are close for both outer and inner orbitals. For core orbitals of water and N_2 BNL OOEs are 5 and 8 eV higher than true KS orbitals, $\sim$25 eV above experimental IPs.[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 $IP_1(\Delta SCF) + \varepsilon_H$. 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 $2a_1$ 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 ith molecular orbital $\psi_i(\mathbf{r})$. The importance of curvature stems from Janak's theorem[55] $\varepsilon_i = \partial E_{gs} / \partial f_i$, so:

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

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 ith orbital. This "fully relaxed" excited state energy for the cation approximates the variational excited state DFT method;[56] so the left hand side of Eq. (1) approximates IP_{N_H+1-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_H+1-i}. When the curvature is positive, Eq. (1) yields $-\varepsilon_i(1) < IP_{N_H+1-i}$, 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: $C_{mi} \equiv (\partial^2 E_{gs} / \partial f_m \partial f_i) = (\partial \varepsilon_m / \partial f_i) = (\partial \varepsilon_i / \partial f_m)$. For clarity, we assume closed shell molecules and we suppress the spin designation for the orbitals $\psi_i(\mathbf{r})$ and OOEs. The Hamiltonian $\hat{H}$ is given by $\delta E_{gs} / [\delta \psi_i(\mathbf{r})] = \hat{H} \psi_i(\mathbf{r})$ and the density matrix is

$\Sigma_i f_i \psi_i(\mathbf{r}) \psi_i(\mathbf{r}')$. 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[57] $\partial \psi_k(\mathbf{r}) / \partial f_i = \Sigma_{j \neq k} \omega_{kj}^{-1} A_{(jk)}^i \psi_j(\mathbf{r})$, where $A_{(jk)}^i \equiv \langle \psi_j | \partial \hat{H} / \partial f_i | \psi_k \rangle$ and $\omega_{kj} = \varepsilon_k - \varepsilon_j$; in particular $C_{mi} = A_{(mm)}^i$. Now, $\partial \hat{H} / \partial f_i$ not only creates the matrix elements $A_{(jk)}^i$ but also depends on them and from this,

$$A_{(nm)}^i = \sum_{jk} (R^{-1})_{(nm)(jk)} W_{(jk)(ii)}, \qquad (2)$$

where the W matrix corresponds to linear response kernel,

$$W_{(jk)(mn)} = \int \int d^3r d^3r' \left[\left(\frac{1}{\mathbf{r} - \mathbf{r}'} + f_{XC}(\mathbf{r}, \mathbf{r}') \right) \psi_j(\mathbf{r}) \psi_n(\mathbf{r}') \right. $$
$$\left. - u(|\mathbf{r} - \mathbf{r}'|) \psi_j(\mathbf{r}') \psi_n(\mathbf{r}) \right] \psi_m(\mathbf{r}') \psi_k(\mathbf{r}). \qquad (3)$$

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

$$R_{(jk)(mn)} = \delta_{(jk)(mn)} + \omega_{nm}^{-1} (f_n - f_m) W_{(jk)(mn)}. \qquad (4)$$

In Eq. (3), $f_{XC}(\mathbf{r}, \mathbf{r}') = \delta v_{XC}[n](\mathbf{r}) / \delta n(\mathbf{r}')$ is the XC kernel and $v_{XC}[n](\mathbf{r})$ 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 $u(r) = \text{erf}(\gamma r)/r$ for RSH (BNL) DFs (in this latter case $v_{XC}[n](\mathbf{r})$ is dependent on the range-parameter γ 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 $W_{(mn)(jk)}$ in Eq. (4) except for same-pair interactions, when $(mn) = (kj)$. In this case $A_{(nm)}^i = W_{(nm)(ii)} / R_{(mn)(mn)}$ and in particular,

$$C_{mi} = A_{(mm)}^i \approx W_{(mm)(ii)}. \qquad (5)$$

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

$$C_{ii} \approx \int \int d^3r d^3r' [\bar{u}(|\mathbf{r} - \mathbf{r}'|) + f_{XC}(\mathbf{r}, \mathbf{r}')] \psi_i(\mathbf{r})^2 \psi_i(\mathbf{r}')^2, \qquad (6)$$

where $\bar{u}(r) = r^{-1} - u(r)$. For the HF theory both f_{XC} and $\bar{u}(r)$ vanish and thus $C_{ii} \approx 0$, a result corroborated for $i = N_H$ in calculations, showing small curvature, only slightly negative.[31,54,58,59] For local/semilocal hybrid DFs, $\bar{u}(r) = (1 - \lambda)/r$ ($\lambda = 0$, local/semilocal and $\lambda = 0.2$, B3LYP) and $f_{XC}(\mathbf{r}, \mathbf{r}') \propto \delta(\mathbf{r} - \mathbf{r}')$, leading to $W_{(ii)(ii)}$ dominated by positive Hartree SR energy for orbital $\psi_i(\mathbf{r})$. This gives significant positive curvature, within semilocal DFs as corroborated by numerical calculations.[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 $f_{XC}(\mathbf{r}, \mathbf{r}')$ 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 $C_{ii} \approx 0$ holds well as seen in numerical calculations.[31,54] In BNL curvatures are small but not exactly zero, thus requiring γ-tuning to have the *initial* slope $\delta E_{gs}/\delta f_H|_{f_H=1}$ equal to the *average* slope $-IP_1 = E_{gs}[N] - E_{gs}[N-1]$.

Summarizing, we gave numerical and theoretical evidence suggesting that *ab initio* motivated γ-tuned BNL enables that of Koopmans' approach using OOEs to approximate IPs to good accuracy. The tuning procedure was found essential for quantitative predictions in other "tough" problems for DFT and TDDFT.[16,43–46]

Supplemental material is available:[61] 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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