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Indirect-path methods for atomic and molecular energies, and new Koopmans theorems

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Staircase and *ladder* methods are proposed for atomic and molecular total and dissociation energies. In both methods, the energies are generated by employing *indirect paths* via information obtained from effective potentials. In the staircase method, the energies are determined in steps by successive alternations of electron and proton removals. Within the Hartree-Fock (HF) staircase formulation, the energy for electron removal is taken as the negative of the highest-occupied orbital energy, and the energy for proton removal is obtained as the difference of conventional HF total-energy expectation values. The HF staircase total and dissociation energies are significantly superior to the traditional HF values. In the ladder method, total energies are obtained by summing successive highest-occupied orbital energies for fixed nuclei. Both methods are useful within more advanced many-body theories and are *exact* within exact Kohn-Sham density-functional theory where the magnitude of the highest-occupied orbital energy *equals* the experimental ionization energy. Self-interaction-corrected density-functional results are presented. We assert two new Koopmans theorems: (1) the energy ε of the highest-occupied HF orbital would give the experimental ionization energy I if the exact ground-state wave function were free of single excitations out of this orbital, and (2) $\varepsilon = -I$ when the exact correlation potential, $v_c([n];\mathbf{r})$, is added to the Fock potential and self-consistency is achieved in both the HF orbitals and in the density n.

We propose new methods, the *staircase* and *ladder* methods for atomic and molecular total and dissociation energies. In both methods, total electronic energies are generated by employing *indirect paths* via information obtained from effective potentials.[1] In the staircase method, the total electronic energy of an atom or molecule is determined in steps by means of successive alternations of electron and proton removals.[1] Further, it is the heart of this method that the energy for electron removal is computed differently than the energy for proton removal. For instance, within the Hartree-Fock staircase formulation, the energy for electron removal is taken as $-\varepsilon$, the negative of the highest-occupied orbital energy (Koopmans ionization energy),[2] and the energy for proton removal is obtained as the difference of conventional Hartree-Fock total-energy expectation values. For additional examples, within the more sophisticated configuration-interaction (CI) or multiconfiguration self-consistent-field (MC-SCF) formulations,[2] the extended Koopmans ionization energy[3,4] is taken for electron removal, and the energy for proton removal is obtained as the difference of traditional CI or traditional MC-SCF expectation values. Any number of formulations may be used for electron removals and for proton removals. In the ladder method, total energies are obtained by summing successive first ionization energies for fixed nuclei (using, e.g., successive highest-occupied orbital energies).

Tables I and II present staircase results for atomic total energies and for molecular dissociation energies, respectively, as obtained from Hartree-Fock (HF) wave functions. All the Hartree-Fock staircase results in these tables are significantly superior to the corresponding traditional Hartree-Fock values, even though only Hartree-Fock wave functions are employed for the necessary staircase data. In essence, we have obtained approximate correlation energies from Hartree-Fock information.

To illustrate the staircase method, for the Li atom the Hartree-Fock staircase energy, $\bar{E}_{\mathrm{HF}}^{\mathrm{Li}}$, is given by

$$\bar{E}_{\mathrm{HF}}^{\mathrm{Li}} = \varepsilon_{\mathrm{Li}} + (E_{\mathrm{HF}}^{\mathrm{Li}^+} - E_{\mathrm{HF}}^{\mathrm{He}}) + \varepsilon_{\mathrm{He}} + E_{\mathrm{HF}}^{\mathrm{He}^+} , \tag{1}$$

where E_{HF} refers to the traditional Hartree-Fock expectation value. Note that since[2] $\varepsilon < \Delta E_{\mathrm{HF}}$, it follows that $\bar{E}_{\mathrm{HF}} < E_{\mathrm{HF}}$, so that $\bar{E}_{\mathrm{HF}}$ is in the right direction compared with E_{HF}.

For molecules, there are many staircase paths to the total electronic energy, $\bar{E}_{\mathrm{HF}}$. The following path appears to work reasonably well and was used for all the molecules in Table II: All along the path, an electron is only removed from a neutral molecule, and a proton is only removed from the heaviest atom in a molecule with a $+1$ charge. Also, a positive ion is fused into the heaviest atom of the starting neutral molecule of interest when the ion is isoelectronic with this heaviest atom. This allows atomic staircase errors to cancel, in part, molecular staircase errors. For instance, $\bar{E}_{\mathrm{HF}}^{\mathrm{Li}_2}$ is given by

$$\bar{E}_{\mathrm{HF}}^{\mathrm{Li}_2} = \varepsilon_{\mathrm{Li}_2} + (E_{\mathrm{HF}}^{\mathrm{Li}_2^+} - E_{\mathrm{HF}}^{\mathrm{LiHe}}) + \varepsilon_{\mathrm{LiHe}} + (E_{\mathrm{HF}}^{\mathrm{LiHe}^+} - E_{\mathrm{HF}}^{\mathrm{HeHe}}) + \varepsilon_{\mathrm{HeHe}} + (E_{\mathrm{HF}}^{\mathrm{HeHe}^+} - E_{\mathrm{HF}}^{\mathrm{Li}}) + \bar{E}_{\mathrm{HF}}^{\mathrm{Li}} , \tag{2}$$

and $\bar{E}_{\mathrm{HF}}^{\mathrm{H_2O}}$ is given by

$$\bar{E}_{\mathrm{HF}}^{\mathrm{H_2O}} = \varepsilon_{\mathrm{H_2O}} + (E_{\mathrm{HF}}^{\mathrm{H_2O}^+} - E_{\mathrm{HF}}^{\mathrm{H_2N}}) + \varepsilon_{\mathrm{H_2N}} + (E_{\mathrm{HF}}^{\mathrm{H_2N}^+} - E_{\mathrm{HF}}^{\mathrm{O}}) + \bar{E}_{\mathrm{HF}}^{\mathrm{O}} . \tag{3}$$

TABLE I. Total atomic energies: Hartree-Fock staircase. Energies and energy differences are expressed in hartrees.

Atom (N)	Experimental[a] E_{GS}	Traditional Hartree-Fock error[b] $E_{HF}-E_{GS}$	Staircase error $\bar{E}_{HF}-E_{GS}$
He (2)	−2.904	0.042	−0.014
Be (4)	−14.667	0.094	0.024
C (6)	−37.845	0.157	0.031
O (8)	−75.067	0.258	−0.117
Ne (10)	−128.94	0.39	−0.26
Mg (12)	−200.06	0.44	−0.21
Si (14)	−289.37	0.52	−0.17
S (16)	−398.14	0.63	−0.18
Ar (18)	−527.60	0.79	−0.15

[a] Hartree-Fock data taken from E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974). The number shown is the Hartree-Fock energy plus the correlation energy.

[b] Correlation energies from A. Veillard and E. Clementi, J. Chem. Phys. **49**, 2415 (1968), but with the sign of the Lamb-shift correction reversed [H. Stoll and A. Savin (private communication)].

The corresponding dissociation energy, $\bar{D}_{HF}^{H_2O}$, is then obtained from

$$\bar{D}_{HF}^{H_2O} = 2\bar{E}_{HF}^{H} + \bar{E}_{HF}^{O} - \bar{E}_{HF}^{H_2O} \ . \tag{4}$$

We call our method the "staircase method" for the following reasons. For any atom or molecule of interest, consider the total number of electrons as the ordinate of a graph and the total number of protons as the abscissa. The removal of an electron at constant proton number is thus a vertical transition down a step, while the removal of a proton at constant electron number is a horizontal transition along a step. (The HF "ladder method" corresponds to the removal of only electrons, not protons; only ε's are employed, not ΔE_{HF}'s. Thus far, we have found the HF ladder method to be not quite as generally effective as the HF staircase method.)

TABLE II. Molecular dissociation energies: Hartree-Fock staircase. Dissociation energies (energy to split the molecule completely into atoms) are expressed in hartrees. All dissociation energies were computed at the experimental geometries.

Molecule	Traditional[a] Hartree-Fock D_{HF}	Experimental[b] D	Staircase[a] $\bar{D}_{HF}$
H_2	0.132	0.175	0.164
Li_2	0.007	0.038	0.030
B_2	0.052	0.11	0.070
C_2	0.117	0.228	0.160
N_2	0.174	0.364	0.269
H_2O	0.242	0.371	0.418
NH_3	0.313	0.473	0.495
CH_4	0.521	0.669	0.669

[a] A 6-311G** (as described in Ref. 5) Gaussian basis set was employed and unrestricted antisymmetric product calculations were performed for all species. Near Hartree-Fock quality was always achieved. All the molecules listed in this table were taken to be spin singlets, except for the triplet B_2.

[b] The experimental dissociation energies (and geometries) for the dimers were taken from G. S. Painter and F. W. Averill, Phys. Rev. B **26**, 1781 (1982). Experimental dissociation energies for the polyatomic molecules were taken from W. J. Hehre, L. Radom, P. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986). The geometries of the polyatomics were taken from pages F-217 and F-218 in *Handbook of Chemistry and Physics,* 57th ed. (CRC Press, Cleveland, 1976).

In the construction of Table II, a 6-311G** basis[5] and a completely unrestricted antisymmetric product (Slater determinant) were used for each species along a staircase. Also, the experimental geometry of the starting molecule of interest was employed for each intermediate species and consistency in spin multiplicity was maintained all along a staircase. For example, if removal of the highest-occupied orbital from a neutral species yielded a triplet for the "frozen" remaining antisymmetric product, then the subtraction of two Hartree-Fock triplet energies was used for the removal of the next proton, and the next electron was removed from a triplet even if the triplet was not the multiplicity of the ground state.

Why does the staircase method work as well as it does with only Hartree-Fock-quality wave functions? First of all, most of the removal energy along the staircase is associated with the horizontal parts; in the absence of certain zero-order degeneracies[6,7] these isoelectronic energy changes are given exactly through second order[6,7] by Hartree-Fock wave functions. For the vertical parts, a given $|\varepsilon|$ typically deviates from the corresponding experimental ionization energy, I, by about 10%. That the error is not typically higher is usually explained[2] by the partial cancellation of relaxation effects and correlation effects. An additional explanation will now be presented.

It is well known, from Brillouin's theorem,[2] that singly excited antisymmetric products (determinants) make very small contributions to the exact ground-state wave function.[8] This is so because any linear combination of the Hartree-Fock determinant with a singly-excited determinant yields no more than a single determinant, and we know that the Hartree-Fock wave function is itself the best possible single determinant. The major corrections to the Hartree-Fock wave function thus arise from double or multiple excitations. With this in mind, the relative success of the ε's follows, in part, from one of our new Koopmans theorem which we now state.

Unless prohibited by symmetry, $|\varepsilon|$ would *equal* I if the exact ground-state wave function were to contain no antisymmetric product obtained by replacement of the highest-occupied orbital in the Hartree-Fock ground state (that is, if the ground-state wave function were free of single excitations out of the highest-occupied Hartree-Fock orbital).

To outline the proof of the theorem, consider the Li^+ ground-state wave function, $\Psi_{\text{Li}^+}(x_1,x_2)$. It can be shown that, with $r_3 \rightarrow \infty$,

$$\Psi_{\text{Li}^+}(x_1,x_2) = B(r_3)[A\phi_1^{\text{HF}}(x_1)\phi_2^{\text{HF}}(x_2)] \times \exp\{[(2I)^{\frac{1}{2}} - (2|\varepsilon|)^{\frac{1}{2}}]r_3\} + \cdots , \quad (5)$$

where $B(r_3)$ does not behave exponentially, A is an antisymmetrizer, ϕ_1^{HF} and ϕ_2^{HF} are the two lowest occupied spin orbitals of the Hartree-Fock wave function for neutral Li, I is the ionization energy of Li, and ε is the energy of the highest-occupied spin orbital of Li, ϕ_3^{HF}. The term shown on the right-hand side of Eq. (5) is part of a complete configuration-interaction expansion[2] for $\Psi_{\text{Li}^+}(x_1, x_2)$. We start with the complete CI expansion for the ground state of neutral Li, $\Psi_{\text{Li}}(x_1,x_2,x_3)$. We choose one of the terms in the expansion to be the Hartree-Fock ground state of Li, $A\phi_1^{\text{HF}}(x_1)\phi_2^{\text{HF}}(x_2)\phi_3^{\text{HF}}(x_3)$. As implied by previous studies,[9-14] to form $\Psi_{\text{Li}^+}(x_1,x_2)$ from $\Psi_{\text{Li}}(x_1,x_2,x_3)$, we then take $r_3 \rightarrow \infty$ in each CI term of $\Psi_{\text{Li}}(x_1,x_2,x_3)$ and multiply the resultant function by $D(r_3)\exp[(2I)^{1/2}r_3]$, $r_3 \rightarrow \infty$, the inverse of the form of the asymptotic decay[9-15] of the square-root of the electron density of Li, where $D(r_3)$ does not behave exponentially. Finally, the factor $\exp[-(2|\varepsilon|)^{1/2}r_3]$ in the term shown on the right-hand side of Eq. (5) arises from the asymptotic decay[16] of $\phi_3^{\text{HF}}(x_3)$.

Now, assume that Ψ_{Li} contains no singly-excited antisymmetric products with respect to replacement of ϕ_3^{HF}. Then the term shown in Eq. (5) would be the only one containing $A\phi_1^{\text{HF}}(x_1)\phi_2^{\text{HF}}(x_2)$, so that there would be no possibility of the cancellation of this shown term as $r_3 \rightarrow \infty$. This means that $\Psi_{\text{Li}^+}(x_1,x_2)$ would blow up if $|\varepsilon| < I$, which is absurd. On the other hand, $A\phi_1^{\text{HF}}(x_1)\phi_2^{\text{HF}}(x_2)$ would make absolutely no contribution to $\Psi_{\text{Li}^+}(x_1,x_2)$ if $|\varepsilon| > I$, which is also absurd [unless $A\phi_1^{\text{HF}}(x_1)\phi_2^{\text{HF}}(x_2)$ happens to be of different symmetry than $\Psi_{\text{Li}^+}(x_1,x_2)$]. Hence, $|\varepsilon| = I$, and $B(r_3 \rightarrow \infty) = \text{const}$.

As a further test of the staircase method, we have determined the H_2 dissociation energy from a two-configurational MC-SCF wave function.[17] The total staircase (or ladder) H_2 energy is obtained simply by adding the electron removal energy, as computed from the MC-SCF wave function by the extended Koopmans approach,[3,4] to the total energy[18] of H_2^+. The resultant MC-SCF staircase dissociation energy turns out to be in error by only +0.007 a.u. This is significantly superior to −0.022 a.u., the error obtained by the traditional MC-SCF expectation value. As a generalization of our first new Koopmans theorem, it can be shown that if the exact ground-state wave function were free of single excitations out of the MC-SCF wave function then the extended Koopmans ionization energy would equal the experimental ionization energy.

It should be observed that the staircase and ladder methods would yield *exact* total energies within the exact Kohn-Sham density-functional theory.[19] This observation follows from the ionization potential theorem:[9,11,20,21] The magnitude of the highest-occupied orbital energy in this theory *equals* the first ionization energy. From just the exact Kohn-Sham one-electron potentials, the exact ground-state energy could be constructed by moving down the ladder. Whether or not this method yields accurate total energies from *approximate* density functionals depends sensitively upon whether or not the approximate Kohn-Sham potential has the correct long-range behavior; poor results for atoms are obtained with the local-spin-density approximation,[19] but good ones with the self-interaction correction (SIC).[20,22] Table III gives staircase and ladder SIC results, including the particularly accurate staircase SIC-HF energies. Almost all of the indirect SIC results are superior to the corresponding direct SIC

TABLE III. Total atomic energies: SIC density functional. Consult Ref. 22 for the SIC formulation. The error, in hartrees, is the calculated value minus the experimental value as given in Table I. In the last column, highest-occupied SIC eigenvalues are taken for electron removals and Hartree-Fock expectation values are taken for proton removals.

Atom (N)	Direct error (SIC)	Ladder error (SIC)	Staircase error (SIC)	Staircase error (SIC-HF)
He (2)	−0.015	−0.044	−0.044	−0.044
Be (4)	−0.027	−0.033	−0.045	−0.024
C (6)	−0.085	−0.010	−0.065	−0.006
O (8)	−0.187	0.006	−0.160	−0.034
Ne (10)	−0.34	−0.04	−0.35	−0.12
Mg (12)	−0.47	0.13	−0.46	−0.11
Si (14)	−0.59	0.32	−0.54	−0.04
S (16)	−0.70	0.53	−0.62	0.02
Ar (18)	−0.82	0.78	−0.71	0.09

results. Furthermore, the indirect-path energies, obtained from the exchange-correlation potentials, v_{xc}, must match the traditional direct energies obtained from the corresponding exchange-correlation energies, E_{xc}, if the density functionals are extremely accurate. Hence, we recognize a severe test upon and a way to improve upon approximate density functionals. In any case, the ladder construction should be especially useful with certain accurate direct approximations to v_{xc} (Refs. 22 and 23) which are not derived from any approximate E_{xc}.[23]

One actually need not know the whole local Kohn-Sham potential to obtain the exact first ionization energy. As a corrollary of the formalisms of Kohn and Sham (Sec. II B),[19] and of Baroni and Tuncel,[24] only knowledge of the exact correlation potential is necessary. This brings us to our second new Koopmans theorem.

$\varepsilon=-I$ when ε is obtained from a Hartree-Fock calculation where the external potential is modified so as to consist of the ordinary Coulomb potential of interest, $v(\mathbf{r})$, plus the exact correlation potential, $v_c([n_{\mathrm{GS}}];\mathbf{r})$, where n_{GS} is the true interacting ground-state density for $v(\mathbf{r})$. In other words, $\varepsilon=-I$ when $v_c([n];\mathbf{r})=\delta E_c/\delta n(\mathbf{r})$ is added to the Fock potential and self-consistency is achieved in both the HF orbitals and in n.

This new Koopmans theorem follows directly from the fact that Baroni and Tuncel[24] have shown that n_{GS} is yielded by that single determinant which minimizes

$$\left\langle T+V_{e\text{-}e}+\sum_i v(\mathbf{r}_i)+\sum_i v_c([n_{\mathrm{GS}}];\mathbf{r}_i)\right\rangle ;$$

we already know that I controls the long-range behavior of n_{GS}.[9-15]

For most practical purposes, a first-order correction,[25] $\int v_c([n_{\mathrm{HF}}];\mathbf{r})\,|\phi_{\mathrm{HF}}(\mathbf{r})|^2 d\mathbf{r}$, to the ordinary Koopmans ionization energy would suffice if v_c were known accurately enough, where ϕ_{HF} is the highest-occupied HF orbital of $v(\mathbf{r})$. (For most closed-shell systems, the correct v_c must have a positive piece.[25] In contrast, the v_c of the local-spin-density approximation[19] is negative everywhere, so that its first-order correction would often be in the wrong direction.[25])

Baroni and Tuncel[24] do not quite use the standard density-functional definition of E_c. To employ the standard definition,[26] simply perform iterative modified[27] Talman-like calculations.[28] That is, minimize[27]

$$\langle\Phi\,|\,T+V_{e\text{-}e}+\sum_i v(\mathbf{r}_i)+\sum_i v_c([n];\mathbf{r}_i)\,|\,\Phi\rangle$$

until self-consistency is achieved in n, with the constraint that each trial Φ is an eigenstate for some local potential. The optimizing local potential gives I because the minimizing Φ is the exact Kohn-Sham determinant for the interacting system of interest.

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