J. Phys. Chem. A **2006,** *110,* 12005−12009 **12005**

Koopmans' Theorem for Large Molecular Systems within Density Functional Theory

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Received: June 13, 2006; In Final Form: August 19, 2006

It is shown that in density functional theory (DFT), Koopmans' theorem for a large molecular system can be stated as follows: The ionization energy of the system equals the negative of the highest occupied molecular orbital (HOMO) energy plus the Coulomb electrostatic energy of removing an electron from the system, or equivalently, the ionization energy of an N-electron system is the negative of the arithmetic average of the HOMO energy of this system and the lowest unoccupied molecular orbital (LUMO) energy of the ($N - 1$)-electron system. Relations between this DFT Koopmans' theorem and its existing counterparts in the literature are discussed. Some of the previous results are generalized and some are simplified. DFT calculation results of a fullerene molecule, a finite single-walled carbon nanotube and a finite boron nitride nanotube are presented, indicating that this Koopmans' theorem approximately holds, even if the orbital relaxation is taken into consideration.

In the Hartree−Fock (HF) method, Koopmans' theorem[1] provides a convenient way to estimate the ionization energy of a molecular system: The energy needed to remove an electron from a certain single-particle state approximately equals the negative of the eigen-energy of that state, provided the corresponding orbital is a canonical one and there is no state relaxation of the remaining electrons. Because electronic structure calculations based on Kohn−Sham (KS) density functional theory (DFT)[2,3] are more efficient and accurate, the DFT version of Koopmans' theorem naturally becomes an interesting topic. Here one problem is that the single-electron states in DFT and their energies are related to a fictitious noninteracting electron system, hence the KS orbitals and levels are sometimes believed to lack physical implications. Nevertheless, Janak[4] proved that in DFT, $\partial E/\partial n_i = \epsilon_i$, where E is the total energy corresponding to the arbitrary (not restricted to integers) occupation n_i of KS orbital ψ_i with energy ϵ_i. Therefore the total energy difference between the N- and ($N - 1$)-electron systems is

$$E(N) - E(N-1) = \int_0^1 \epsilon_N(n)\, \mathrm{d}n \tag{1}$$

where $\epsilon_N(n)$ is the Nth KS level whose occupation number is n, and $0 \leq n \leq 1$. Accordingly Janak claimed that for extended systems

$$I(N) = E(N-1) - E(N) = -\epsilon_N \tag{2}$$

where $I(N)$ and ϵ_N are the ionization energy and the highest occupied molecular orbital (HOMO) level of the N-electron system. This is because $\epsilon_N(n)$ only changes infinitesimally when n varies from 0 to 1, corresponding to the ($N - 1$)- and N-electron systems, respectively. Hence in DFT, Koopmans' theorem holds for HOMO of an extended system. Later Harris and Ballone[5] gave a further consideration of the function $\epsilon_N(n)$ and found that the more accurate DFT Koopmans' theorem within local density approximation (LDA) is

$$I(N) = -\epsilon_N + \frac{1}{2}\left\{\int\!\!\int \frac{e^2|\psi_N(\vec{r})|^2|\psi_N(\vec{r}\,')|^2}{4\pi\epsilon_0|\vec{r} - \vec{r}\,'|}\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' + \int\left|\psi_N(\vec{r})\right|^4 \frac{\partial\mu_{\mathrm{xc}}(\rho(\vec{r}))}{\partial\rho}\,\mathrm{d}\vec{r}\right\} \tag{3}$$

where $\psi_N(\vec{r})$ is the Nth KS orbital, and $\mu_{\mathrm{xc}}(\rho(\vec{r}))$ is the LDA exchange-correlation potential. On the other hand, there are conclusions that eq 2 exactly holds for finite systems.[6,7] The DFT Koopmans' theorem thus has been an issue open to discussion,[6−13] and one reason for the discrepancy might be the different extensions of DFT to systems with a fractional number of electrons.[11]

In this brief report, we show that for a large molecular system, DFT Koopmans' theorem seems to be

$$I(N) = E(N-1) - E(N) = -\epsilon_N + \frac{e^2}{2C} \tag{4}$$

where C is the capacitance of the molecular system and e is the elementary charge. Hence the ionization energy of the system equals the negative of the HOMO energy *plus* the classical Coulomb electrostatic energy needed to remove an electron from the system. Janak's extended systems then have a large capacitance so that $e^2/2C \ll |\epsilon_N|$. Moreover, it is shown that the added term in eq 3 by Harris and Ballone approximately equals $e^2/2C$. In addition, if we eliminate the parameter C from eq 4, then equivalently the ionization energy is the arithmetic average of the HOMO energy of the N-electron system and the lowest unoccupied molecular orbital (LUMO) energy of the ($N - 1$)-electron system. DFT calculation results of a fullerene C_{60}, a finite (6, 0) single-walled carbon nanotube (SWCNT) C_{96}, and a finite (6, 0) boron nitride (BN) nanotube $B_{48}N_{48}$ are presented, which confirms this DFT Koopmans' theorem. On the other hand, because we mainly consider systems with an integer number of electrons, the different extensions of DFT to systems with a fractional number of electrons and related debate are not addressed.

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10.1021/jp063669m CCC: $33.50

In a separate paper,[14] it is proved according to DFT that the Coulomb potential variation in a large molecular system is approximately homogeneous in space if there is a small change of the electron number, from N to N'. This property provides a natural definition of the capacitance of the system, that is,

$$\int \frac{e^2\rho'(\vec{r}\,')}{4\pi\epsilon_0|\vec{r} - \vec{r}\,'|}\,\mathrm{d}\vec{r}\,' - \int \frac{e^2\rho(\vec{r}\,')}{4\pi\epsilon_0|\vec{r} - \vec{r}\,'|}\,\mathrm{d}\vec{r}\,' = \frac{(N' - N)e^2}{C} \tag{5}$$

where $\rho(\vec{r})$ and $\rho'(\vec{r})$ are the electron densities of the N- and N'-electron systems, respectively. Within this approximation, it is further proved that the DFT total energy difference between the two systems is

$$E(N') - E(N) = \begin{cases} \displaystyle\sum_{i=N+1}^{N'} \epsilon_i + \frac{(N' - N)^2 e^2}{2C} & (N' > N) \\ \displaystyle -\sum_{i=N'+1}^{N} \epsilon_i + \frac{(N - N')^2 e^2}{2C} & (N' < N) \end{cases} \tag{6}$$

and all the KS levels shift almost identically, that is,

$$\epsilon_i' - \epsilon_i = \frac{(N' - N)e^2}{C} \tag{7}$$

where ϵ_i and ϵ_i' are the ith KS levels of the N- and N'-electron systems, respectively. For a quantum dot (QD), eq 6 is actually the constant interaction (CI) model.[15] For $N' = N - 1$, eq 6 leads to eq 4. If we designate the Nth KS level of the $(N - 1)$-electron system as ϵ_N', according to eq 7, the capacitance of the system is related to ϵ_N and ϵ_N' by

$$\epsilon_N' - \epsilon_N = -\frac{e^2}{C}. \tag{8}$$

Equation 4 can then be written as

$$I(N) = E(N - 1) - E(N) = -\frac{1}{2}(\epsilon_N + \epsilon_N') \tag{9}$$

It also can be proved[14] that in a large molecular system, approximately

$$\int \frac{e^2|\psi_N(\vec{r}\,')|^2}{4\pi\epsilon_0|\vec{r} - \vec{r}\,'|}\,\mathrm{d}\vec{r}\,' + |\psi_N(\vec{r})|^2 \frac{\partial\mu_{\mathrm{xc}}(\rho(\vec{r}))}{\partial\rho} = \frac{e^2}{C} \tag{10}$$

Multiplying eq 10 by $|\psi_N(\vec{r})|^2$ and then calculating the integration with respect to $\vec{r}$, one gets

$$\int\int \frac{e^2|\psi_N(\vec{r})|^2|\psi_N(\vec{r}\,')|^2}{4\pi\epsilon_0|\vec{r} - \vec{r}\,'|}\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' + \int |\psi_N(\vec{r})|^4 \frac{\partial\mu_{\mathrm{xc}}(\rho(\vec{r}))}{\partial\rho}\,\mathrm{d}\vec{r} = \frac{e^2}{C}\int |\psi_N(\vec{r})|^2\,\mathrm{d}\vec{r} = \frac{e^2}{C} \tag{11}$$

because $\int |\psi_N(\vec{r})|^2\,\mathrm{d}\vec{r} = 1$. Hence eqs 3 and 4 are the same for large molecular systems.

TABLE 1: Calculated Total Energy $E(N)$, Ionization Energy $I(N) = E(N - 1) - E(N)$, HOMO Energy ϵ_N of the N-Electron System, LUMO Energy ϵ_N' of the $(N - 1)$-Electron System, the Quantity $-(\epsilon_N + \epsilon_N')/2$, and the Quantity $-\epsilon_N + e^2/2C$, for a Fullerene C_{60} Molecule[a]

N	$E(N)$ (eV)	$E(N-1) - E(N)$ (eV)	ϵ_N (eV)	ϵ_N' (eV)	$-(\epsilon_N + \epsilon_N')/2$ (eV)	$-\epsilon_N + e^2/2C$ (eV)
355	−62088.334	23.765	−22.150	−25.321	23.736	23.777
356	−62108.563	20.229	−18.698	−21.851	20.275	20.318
357	−62125.664	17.101	−15.557	−18.698	17.128	17.170
358	−62139.648	13.984	−12.427	−15.557	13.992	14.033
359	−62150.525	10.877	−9.310	−12.427	10.869	10.910
360	−62158.306	7.781	−6.204	−9.310	7.757	7.797
361	−62161.286	2.980	−1.476	−4.551	3.014	3.057
362	−62161.222	−0.064	1.587	−1.476	−0.056	−0.014
363	−62158.125	−3.096	4.637	1.587	−3.112	−3.071
364	−62151.766	−6.359	7.841	4.807	−6.324	−6.282
365	−62142.404	−9.362	10.862	7.841	−9.352	−9.310
366	−62130.050	−12.354	13.872	10.862	−12.367	−12.328

[a] N is the electron number, and $N = 360$ corresponds to the neutral system.

TABLE 2: Calculated Total Energy $E(N)$, Ionization Energy $I(N) = E(N - 1) - E(N)$, HOMO Energy ϵ_N of the N-Electron System, LUMO Energy ϵ_N' of the $(N - 1)$-Electron System, the Quantity $-(\epsilon_N + \epsilon_N')/2$, and the Quantity $-\epsilon_N + e^2/2C$, for a (6, 0) SWCNT C_{96}[a]

N	$E(N)$ (eV)	$E(N-1) - E(N)$ (eV)	ϵ_N (eV)	ϵ_N' (eV)	$-(\epsilon_N + \epsilon_N')/2$ (eV)	$-\epsilon_N + e^2/2C$ (eV)
569	−99324.582	24.344	−23.267	−25.452	24.360	24.340
570	−99346.316	21.735	−20.561	−23.267	21.914	21.955
571	−99364.862	18.545	−17.327	−19.771	18.549	18.571
572	−99380.931	16.069	−14.874	−17.263	16.069	16.102
573	−99394.540	13.609	−12.546	−14.780	13.663	13.722
574	−99405.952	11.413	−10.261	−12.545	11.403	11.431
575	−99414.903	8.950	−7.980	−10.143	9.062	9.105
576	−99421.549	6.646	−5.456	−7.980	6.718	6.741
577	−99425.646	4.097	−3.247	−5.282	4.265	4.294
578	−99427.373	1.726	−0.595	−3.247	1.921	1.960
579	−99426.664	−0.709	1.770	−0.404	−0.683	−0.611
580	−99423.753	−2.911	4.031	1.798	−2.915	−2.876
581	−99418.385	−5.367	6.614	4.203	−5.409	−5.376
582	−99410.832	−7.553	8.660	6.614	−7.637	−7.598
583	−99401.110	−9.723	10.891	8.746	−9.819	−9.739

[a] N is the electron number, and $N = 576$ corresponds to the neutral system.

By using DFT based DMol3 code,[16,17] we calculated the total energies and KS levels of a fullerene C_{60} molecule, a finite (6, 0) SWCNT containing 96 carbon atoms, and a finite (6, 0) BN nanotube containing 48 boron atoms and 48 nitrogen atoms. All the electrons were included in the calculations, and we adopted the double numerical plus polarization (DNP) atomic orbital basis set, the PBE general gradient approximation (GGA) to the exchange-correlation energy,[18] and the spin-unrestricted single-electron wave functions. The atomic structure of the C_{60} was determined according to experimental data; that is, the single- and double-bond lengths were chosen to be 1.45 and 1.40 Å, respectively.[19] Our calculations gave the removal energy of the electron from the HOMO of the neutral C_{60} to be 7.78 eV, in good agreement with the experimental photoelectron spectrum results of both solid- and gas-phase fullerene.[20,21] The structure optimization calculations led to the neutral finite-length (6, 0) SWCNT with C−C bond lengths ranging from 1.404 to 1.449 Å, and the neutral finite-length (6, 0) BN nanotube with B−N bond lengths ranging from 1.436 to 1.489 Å, in agreement with the generally adopted data.[22,23]

Tables 1−3 list the calculated total energy $E(N)$, ionization energy $I(N) = E(N - 1) - E(N)$, HOMO energy ϵ_N of the N-electron system, LUMO energy ϵ_N' of the $(N - 1)$-electron system, the quantity $-(\epsilon_N + \epsilon_N')/2$, and the quantity $-\epsilon_N + e^2/2C$ for the C_{60} molecule, the SWCNT, and the BN nanotube, respectively. It is shown that $I(N) > -\epsilon_N$ and there are relatively large deviations between the ionization energy and the negative of the HOMO energy. Only after the Coulomb electrostatic energy $e^2/2C$ is added to the negative of the HOMO energy does the sum of the two approximately equal the ionization energy.

TABLE 3: Calculated Total Energy $E(N)$, Ionization Energy $I(N) = E(N - 1) - E(N)$, HOMO Energy ϵ_N of the N-Electron System, LUMO Energy ϵ'_N of the $(N - 1)$-Electron System, the Quantity $-(\epsilon_N + \epsilon'_N)/2$, and the Quantity $-\epsilon_N + e^2/2C$, for a (6, 0) BN Nanotube $B_{48}N_{48}$[a]

N	$E(N)$ (eV)	$E(N-1) - E(N)$ (eV)	ϵ_N (eV)	ϵ'_N (eV)	$-(\epsilon_N + \epsilon'_N)/2$ (eV)	$-\epsilon_N + e^2/2C$ (eV)
569	−103893.294	23.862	−22.657	−24.942	23.800	23.828
570	−103914.803	21.509	−20.309	−22.657	21.483	21.497
571	−103933.922	19.119	−17.939	−20.309	19.124	19.130
572	−103950.629	16.708	−15.554	−17.939	16.747	16.747
573	−103964.910	14.281	−13.149	−15.550	14.350	14.341
574	−103976.743	11.833	−10.720	−13.149	11.935	11.911
575	−103986.093	9.349	−8.254	−10.720	9.487	9.441
576	−103992.907	6.814	−5.725	−8.254	6.990	6.903
577	−103997.084	4.177	−2.901	−5.575	4.238	4.067
578	−103998.527	1.443	−0.282	−2.901	1.592	1.436
579	−103997.412	−1.116	2.156	−0.282	−0.937	−1.010
580	−103993.851	−3.561	4.523	2.156	−3.340	−3.385
581	−103987.903	−5.948	7.011	4.785	−5.898	−5.884
582	−103979.633	−8.269	9.212	7.011	−8.112	−8.105
583	−103969.102	−10.531	11.762	9.588	−10.675	−10.676
584	−103956.390	−12.713	13.824	11.762	−12.793	−12.779

[a] N is the electron number, and $N = 576$ corresponds to the neutral system.

Another approximate result along with eqs 5−7 is that KS orbitals will not change when the electron number changes from N to N'.[14] On the analogy of HF theory and from the single-electron point of view, this may correspond to the fact that when an electron is removed from the system, there is no relaxation of the remaining electrons. We note that the nonrelaxation of the single-electron orbitals leads to exactly identical shifts of all KS levels, as is expressed by eq 7. Thus in real calculations, the orbital relaxation can be appraised by the nonuniformity of the KS level shift. Figure 1 illustrates the distribution of the KS level shift for the C_{60}, the SWCNT, and the BN nanotube when their electron number increases by 1, from N to $N' = N + 1$, and the distribution ranges are listed in Tables 4−6. For the C_{60}, this range is as small as about 0.1 eV. For the BN nanotube, the range is larger. The relatively large dispersion of the KS level shift may be due to two facts: The first is the different valence electron affinity of boron and nitrogen atoms, and the second is the lower symmetry of the BN nanotube. In both cases the electron relaxation is more pronounced. Nevertheless, despite the orbital relaxation, eq 4 still approximately holds if we take the quantity e^2/C as the average value of the KS level shift. For all the three systems, this quantity in Tables 1−3 is obtained as the average shift of the occupied KS levels. Besides, eq 9 also holds. This may be related to the fact that the large dispersion of the KS level shift is due to the KS orbitals which have much lower energies.

Figure 2 illustrates statistically the variation of the molecular electrostatic potential of the C_{60}, the SWCNT, and the BN nanotube when their electron number increases by one, from N to $N' = N + 1$. The molecular electrostatic potential in the region enclosed by the 0.002 au (1 au = 6.7482 e/Å^3) electron density isosurface was calculated at grid points spaced by 0.1 Å in each of the three directions and the histogram of the potential variation is plotted in Figure 2. Compared with the shift of KS levels, the potential variation is less uniform. However, the average value of the potential variation coincides well with that of the KS level shift and this average value can also be used to obtain the quantity e^2/C.

Although it only approximately holds, eq 5 provides a capacitance definition that conforms with the classical notion.

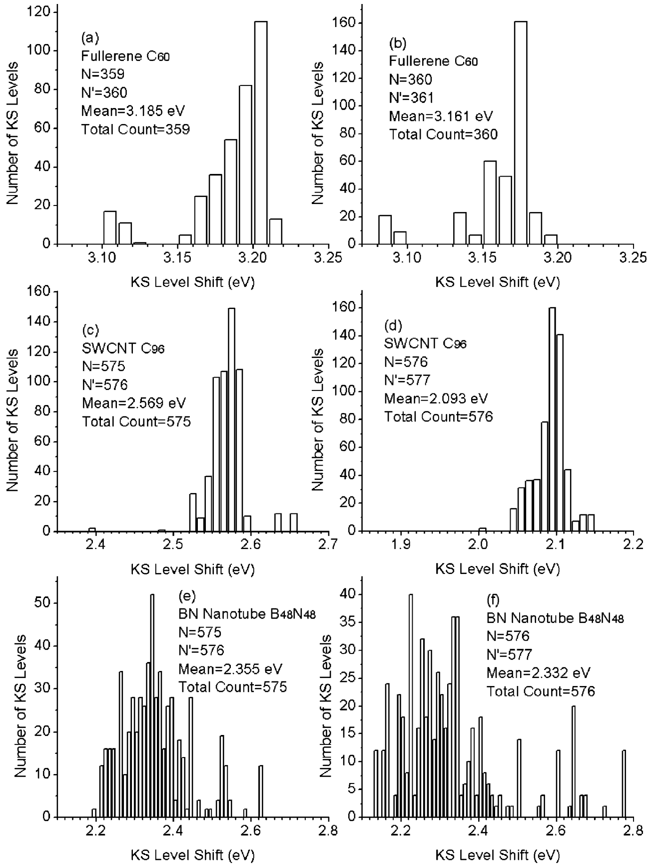

Figure 1. Histograms of the shift of occupied KS levels for a fullerene C_{60} [(a), (b)], a (6, 0) SWCNT C_{96} [(c), (d)], and a (6, 0) BN nanotube $B_{48}N_{48}$ [(e), (f)], when their electron number increases by 1, from N to $N' = N + 1$.

TABLE 4: Minimum, Maximum, Average, and Range of the Shift of All Occupied KS Levels for a Fullerene C_{60} When Its Electron Number Increases by 1, from N to $N' = N + 1$

N	N'	$\min(\epsilon'_i - \epsilon_i)$ (eV)	$\max(\epsilon'_i - \epsilon_i)$ (eV)	$\overline{\epsilon'_i - \epsilon_i}$ (eV)	max − min (eV)
354	355	3.170	3.282	3.254	0.112
355	356	3.152	3.267	3.239	0.115
356	357	3.141	3.254	3.226	0.113
357	358	3.129	3.242	3.212	0.113
358	359	3.117	3.228	3.199	0.111
359	360	3.105	3.216	3.185	0.111
360	361	3.085	3.192	3.161	0.107
361	362	3.063	3.179	3.147	0.116
362	363	3.050	3.166	3.133	0.116
363	364	3.043	3.151	3.118	0.108
364	365	3.021	3.138	3.104	0.117
365	366	3.010	3.125	3.089	0.115

Let $\Delta\rho(\vec{r}) = \rho'(\vec{r}) - \rho(\vec{r})$, eq 5 gives the classical Coulomb potential energy

$$\frac{1}{2}\int\int \frac{e^2\Delta\rho(\vec{r})\,\Delta\rho(\vec{r}\,')}{4\pi\epsilon_0|\vec{r} - \vec{r}\,'|}\,\mathrm{d}\vec{r}\,\mathrm{d}\vec{r}\,' = \frac{(N' - N)^2 e^2}{2C} \qquad (12)$$

The capacitance also leads to the separation of the contributions of the classical Coulomb energy and the quantum mechanics energy level to the ionization energy, as demonstrated by eq 4. This capacitance definition is different from that given by Iafrate

TABLE 5: Minimum, Maximum, Average, and Range of the Shift of All Occupied KS Levels for a (6, 0) SWCNT C_{96} When Its Electron Number Increases by 1, from N to $N' = N + 1$

N	N'	$\min(\epsilon_i' - \epsilon_i)$ (eV)	$\max(\epsilon_i' - \epsilon_i)$ (eV)	$\overline{\epsilon_i' - \epsilon_i}$ (eV)	max − min (eV)
568	569	2.035	2.222	2.145	0.187
569	570	2.686	2.869	2.787	0.183
570	571	2.310	2.591	2.487	0.281
571	572	2.359	2.505	2.455	0.146
572	573	2.281	2.664	2.352	0.383
573	574	2.226	2.604	2.340	0.378
574	575	2.098	2.315	2.250	0.217
575	576	2.392	2.655	2.569	0.263
576	577	2.000	2.146	2.093	0.146
577	578	2.596	2.768	2.730	0.172
578	579	2.226	2.496	2.318	0.270
579	580	2.233	2.458	2.310	0.225
580	581	2.393	2.642	2.476	0.249
581	582	2.044	2.185	2.124	0.141
582	583	2.084	2.865	2.305	0.781

TABLE 6: Minimum, Maximum, Average, and Range of the Shift of All Occupied KS Levels for a (6, 0) BN Nanotube $B_{48}N_{48}$ When Its Electron Number Increases by 1, from N to $N' = N + 1$

N	N'	$\min(\epsilon_i' - \epsilon_i)$ (eV)	$\max(\epsilon_i' - \epsilon_i)$ (eV)	$\overline{\epsilon_i' - \epsilon_i}$ (eV)	max − min (eV)
568	569	2.162	2.704	2.342	0.542
569	570	2.222	2.625	2.375	0.403
570	571	2.208	2.600	2.382	0.392
571	572	2.262	2.585	2.385	0.323
572	573	2.247	2.576	2.384	0.329
573	574	2.276	2.557	2.381	0.281
574	575	2.270	2.532	2.373	0.262
575	576	2.197	2.620	2.355	0.423
576	677	2.134	2.775	2.332	0.641
577	578	2.158	2.713	2.308	0.555
578	579	2.168	2.508	2.293	0.340
579	580	2.160	2.459	2.277	0.299
580	581	2.142	2.374	2.254	0.232
581	582	2.107	2.414	2.214	0.307
582	583	2.068	2.385	2.172	0.317
583	584	1.979	2.613	2.090	0.634

et al.[24] in terms of chemical potentials for atomic-sized structures through the equation

$$\frac{e^2}{C(N)} = \mu(N+1) - \mu(N) = E(N+1) - 2E(N) + E(N-1) \tag{13}$$

where $\mu(N) = E(N) - E(N-1)$ is the chemical potential of the N-electron system. Iafrate et al. also mentioned that according to eq 13 and calculation results,

$$\frac{e^2}{C(N)} = I(N) - A(N) = \epsilon_{N+1} - \epsilon_N + B_0 \tag{14}$$

where $A(N) = E(N) - E(N+1)$ is the electron affinity of the system and B_0 is nearly a constant.[24] On the other hand, according to eq 6, our definition leads to

$$A(N) = -\epsilon_{N+1} - \frac{e^2}{2C} \tag{15}$$

and

$$I(N) - A(N) = \epsilon_{N+1} - \epsilon_N + \frac{e^2}{C} \tag{16}$$

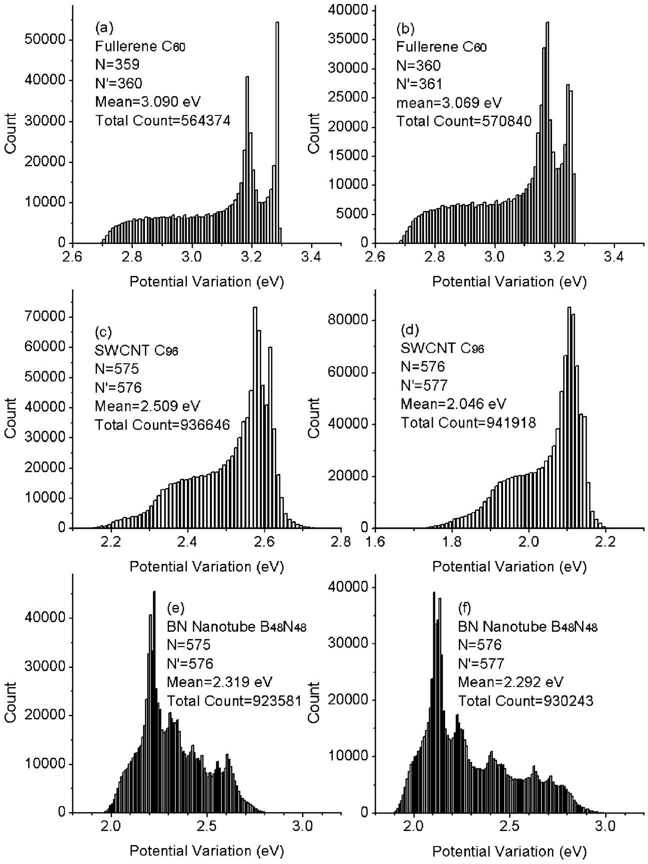

Figure 2. Histograms of the variation of molecular electrostatic potential for a fullerene C_{60} [(a), (b)], a (6, 0) SWCNT C_{96} [(c), (d)], and a (6, 0) BN nanotube $B_{48}N_{48}$ [(e), (f)], when their electron number increases by 1, from N to $N' = N + 1$. The electrostatic potential was calculated in the region enclosed by the 0.002 au electron density isosurface and at grid points spaced by 0.1 Å in each of the three directions.

Thus the constant B_0 now has its physical meaning $B_0 = e^2/C$ by the capacitance definition given in this report. The quantity $e^2/C(N)$ of Iafrate et al., however, is in fact the second difference of the total energy, which has already been defined as the addition energy of a QD.[15] Results may seem clearer and simpler if the capacitance definition given by eq 5 is adopted for a large molecular system. Besides, although the numerical integration is time-consuming, eq 12 provides another way to calculate the quantity e^2/C. Tentative calculations of the C_{60}, the SWCNT, and the BN nanotube demonstrated that e^2/C obtained from eq 12 also makes eq 4 hold well.

For an open-shell N-electron system, there is the result in LDA and GGA that[9,25]

$$\epsilon_N = -\frac{1}{2}[I(N) + A(N)] \tag{17}$$

This equation can be derived from eq 6, under the assumption that the capacitance of the system is a constant. In fact, eq 6 leads to eqs 4 and 15. For an open-shell system, $\epsilon_{N+1} = \epsilon_N$, and adding eqs 4 and 15 together leads to eq 17. Nevertheless, eq 17 is not a general conclusion because it may not hold for a closed-shell structure. For instance, the 360 electrons of the neutral C_{60} molecule constitute a closed-shell system. The orbital 361 belongs to the T_u irreducible representation of the symmetry group I_h, different from the H_u representation of the orbital 360. Thus $\epsilon_{N+1} > \epsilon_N$ and eq 17 does not hold. In fact, $\epsilon_{361} = -4.551$ eV, $\epsilon_{360} = -6.204$ eV, and $-[I(360) + A(360)]/2 = -5.381$

eV (Table 1). The same is true for the closed-shell SWCNT and closed-shell BN nanotube, only the energy-level intervals in these systems are smaller than those in the C_{60}, and the difference between ϵ_N and $-[I(N) + A(N)]/2$ is also smaller. Equation 17 can be a good approximation for large molecular systems with a low symmetry, where the energy-level intervals are small, but may fail for systems with a high symmetry, where the energy-level intervals are large.

If we choose N to be the electron number of the neutral system, eq 6 then gives the relative total energy of the system with an excess charge $(N' - N)e$. For a system with a not very large but approximately constant capacitance, the total energy variation is dominated by the term $(N' - N)^2e^2/2C$, meaning $E(N')$ varies approximately as a quadratic function of N'. At the same time, if the intervals of the KS levels around the HOMO of the neutral system are small, that is, $|\epsilon_{i+1} - \epsilon_i| \ll e^2/C$, eq 7 indicates that approximately the HOMO level of the charged system, $\epsilon'_{N'}$, varies linearly with respect to N'. It is interesting that if the total energy is fitted as a quadratic function of the electron number, then the ionization energy calculated from this function may approximately coincide with the negative of the HOMO level. If the number of excess electrons is small, the fitted quadratic total energy function may lead to ionization energy that agrees very well with the negative of the HOMO level calculated from the fitted linear function, and eq 2 seemingly holds.[26,27] However, the quadratic fitting destroys details of the total energy variation. The conclusion is that eqs 3, 4, and 9 should be the more exact DFT Koopmans' theorem for large molecular systems.

In summary, a more exact and simpler form of Koopmans' theorem for large molecular systems within DFT is given in this brief report. The relations between this Koopmans' theorem and its existing counterparts in the literature are discussed. Some of the previous results are generalized and some are simplified. DFT calculations of a fullerene C_{60} molecule, a finite SWCNT, and a finite BN nanotube verified this Koopmans' theorem.

Acknowledgment. J.L. is grateful to Professor Xun Wang for his assistance. This work was supported by the National Natural Science Foundation of China, the Ministry of Science and Technology of China, and the Postdoctoral Science Foundation of China.

References and Notes

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