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# Principle of Maximum Hardness: An ab-Initio Study†

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In this paper we test the principle of maximum hardness through an accurate quantum chemical calculation. Computations include extensive correlation and relaxation effects for the calculation of ionization potential and electron affinity. The molecule water has been chosen as a primary test case.

## Introduction

The principle of maximum hardness for atomic and molecular systems has been of great recent interest. Hardness  $\eta$  of a system is related to the second derivative of energy with respect to the number of particles  $N$  for constant  $v$  (potential due to nuclei plus external potential) and temperature.<sup>1</sup> The slope of such a curve in this condition is the chemical potential  $\mu$ . The principle states that at constant  $v$  and  $\mu$ , the system will evolve to a state with maximum  $\eta$ . As has been pointed out,<sup>2</sup> this principle justifies a great deal of intuition, too. A rigorous proof of this has also been given by Parr and Chattaraj.<sup>3</sup> This principle has been tested by Pearson and Palke (PP)<sup>4</sup> as well as Datta<sup>5</sup> recently. While Datta used MNDO calculations, PP used ab-initio self-consistent field methods to test the principle. In each of these two cases the hardness and chemical potential were calculated through the independent particle model.  $\eta$  and  $\mu$  are rigorously defined as<sup>1</sup>

$$2\eta = (\delta^2 E / \delta N^2)_{v,T} \quad \mu = (\delta E / \delta N)_{v,T} \quad (1)$$

Using a three point fit, it can be shown that<sup>6</sup>

$$\eta = (IP - EA)/2 \quad \mu = -(IP + EA)/2 \quad (2)$$

where IP refers to the first ionization potential and EA refers to the first electron affinity of the  $N$ -particle system. In each of the earlier two supporting calculations, the Koopmans' approximation has been used to estimate the IP and EA. It is well-known that while these approximations work to a reasonable degree of satisfaction, they often provide even qualitatively wrong results for IP and, in particular, for EA. The failure of Koopmans' theorem is well documented in the literature of quantum chemistry.<sup>7</sup> An exact calculation of  $\eta$  and  $\mu$  through eq 1 is not feasible; however, a calculation of  $\eta$  and  $\mu$  through eq 2 is warranted for a test of the principle. We want to carry out such a test in this paper. We may point out, however, that the rigor of this test is still limited by the fact that eq 2 is an approximate definition of  $\mu$  and  $\eta$ .

## Computational Method

One of the most accurate quantum chemical methods is the one based on the coupled cluster (CC) theory.<sup>8–10</sup> CC methods are recommended for the efficient incorporation of electron correlation and the size extensivity, which are particularly important for extended systems.<sup>9,10</sup> For quasidegenerate systems, it is required to start from a multideterminantal model space. A general multideterminantal model space can avoid the problem of the convergence arising out of the intruder states. The Fock space based multireference CC method has been used to estimate the difference energies like the IPs, EAs, and excitation energies very accurately in a direct manner.<sup>12–14</sup> This dramatically improves these values. In particular, it is well-known that for the EA's the correlation and

relaxation effects significantly affect the results. In Fock space MRCC methods, the restricted Hartree–Fock (RHF) determinant of an  $N$  electron ground state is taken as the core or vacuum and the problem of  $(N - 1)$  or  $(N + 1)$  electron states is reduced to a one hole/one particle problem.  $(N - 1)$  electron problems may be considered as in the 0-particle, 1-hole Fock space sector and  $(N + 1)$  electron problems are in the 1-particle and 0-hole Fock space sector. For  $(N - 1)$  electron states, one constructs a  $(N - 1)$  electron model space consisting of a few one-hole determinants. The model space  $\psi_\mu^0$  can be written as

$$\psi_\mu^{0(0,1)} = \sum_I C_{\mu I} \phi_I \quad (3)$$

$\{\phi_I\}$  is a set of 1-hole determinants. The exact  $(N - 1)$  electron states may be written as

$$\psi_\mu^{(0,1)} = \Omega \psi_\mu^{0(0,1)} = \{e^{T^I}\} \psi_\mu^{0(0,1)} \quad (4)$$

where  $T^I$  is expressed as sum of cluster amplitudes of the 0-hole, 0-particle sector as well as new amplitudes for the 1-hole sector and the curly bracket denotes normal ordering of the operators contained within it. Normal ordering of the ansatz was introduced by Lindgren.<sup>15</sup> The cluster amplitudes of the (0,0) sector are obtained by the projection of Schrodinger's equation for the ground-state problem to the set of  $N$ -particle excited determinants  $\phi^*$ .<sup>8</sup> The cluster amplitudes for the (0,1) sector may be obtained by projection of the Fock space Bloch's equation of the (0,1) sector to the virtual space of determinants  $\phi^*$ . The Bloch equation of the (0,1) sector may be written as

$$(H\Omega - \Omega H_{\text{eff}}^{(0,1)})P^{(0,1)} = 0 \quad (5)$$

Similarly the Bloch equation of the (1,0) sector is

$$(H\Omega - \Omega H_{\text{eff}}^{(1,0)})P^{(1,0)} = 0 \quad (6)$$

We have used an approximation where the cluster amplitudes for the (0,1) or (1,0) sector contain only singly and doubly excited parameters and the ground-state cluster amplitudes are truncated in only a two-body approximation. This model has been sufficient to provide accurate values for medium-sized systems.<sup>12,13</sup> Initially, we carry out a CC calculation with only doubly excited parameters for the ground state. Then we construct a transformed Hamiltonian  $\bar{H}$  as  $\bar{H} = e^{-T(0,0)} H e^{T(0,0)}$  and store only the one- and two-body parts (ignoring higher body components of  $\bar{H}$ ). This is an additional approximation used. However, it is expected that the three body and higher body parts will not change the results significantly. Using the one- and two-body parts of  $\bar{H}$  in CCD approximation, we solve the projection of eq 5 to one- and two-body virtual space of the (0,1) sector, as well as similar projection of eq 6 to the (1,0) sector. These are systems of nonlinear equations furnishing  $T_1^{(0,1)}$ ,  $T_2^{(0,1)}$ ,  $T_1^{(1,0)}$ , and  $T_2^{(1,0)}$  amplitudes. The effective Hamiltonian for the (0,1) and (1,0) problem may be obtained as the  $P$ -space projection of eq 5 and eq 6, respectively. In general,

† N.C.L. Communication No. 5600.

TABLE I: Symmetric Distortion of Water<sup>a</sup>

O-H bond	$\eta_K$	$\mu_K$	$\eta_{Mrcc}$	$\mu_{Mrcc}$
$\pm 0.2^\circ$	0.344 937	-0.150 889	0.296 604	-0.124 596
+0.1	0.353 920	-0.144 830	0.308 309	-0.120 509
+0.02	0.361 007	-0.140 663	0.317 505	-0.117 697
equil <sup>b</sup>	0.362 758	-0.139 727	0.319 887	-0.117 191
-0.02 <sup>c</sup>	0.364 493	-0.138 839	0.322 162	-0.116 608
-0.1	0.371 316	-0.135 760	0.330 955	-0.114 672
-0.2	0.379 500	-0.133 070	0.341 449	-0.113 240
HOH angle				
+5°	0.362 162	-0.138 565	0.319 167	-0.116 170
+1°	0.362 659	-0.139 468	0.319 784	-0.116 943
equil <sup>b</sup>	0.362 758	-0.139 727	0.319 887	-0.117 191
-1°	0.362 832	-0.139 977	0.319 918	-0.117 356
-5°	0.363 022	-0.141 108	0.320 230	-0.118 408

<sup>a</sup> All values are in atomic units (au) except bond angles, which are in degrees. <sup>b</sup> Equilibrium condition when the O-H bond distance is 1.8091 au and the H-O-H bond angle is 104.5°. <sup>c</sup> (+) for stretching and (-) for contraction of the O-H bond.

TABLE II: Asymmetric Distortion of Water<sup>a</sup>

O-H bond	$\eta_K$	$\mu_K$	$\mu_{Mrcc}$	$\mu_{Mrcc}$
0.2	0.357 197	-0.146 466	0.313 773	-0.123 304
0.04	0.362 513	-0.140 019	0.319 508	-0.117 359
0.02	0.362 695	-0.139 801	0.319 762	-0.117 206
equil <sup>b</sup>	0.362 758	-0.139 727	0.319 887	-0.117 191

<sup>a</sup> All values are in atomic units (au). <sup>b</sup> Equilibrium condition in which O-H bond distance is taken to be 1.8091 au and H-O-H bond angle is 104.5°.

the eigenvalues of the effective Hamiltonian furnish the energies of the  $(N-1)/(N+1)$  electron systems. If the closed diagrams pertaining to the ground-state energy are dropped from the construction of  $\bar{H}$ , the eigenvalues of  $H_{eff}^{(0,1)}$  and  $H_{eff}^{(1,0)}$  reflect the ionization and electron affinity of the  $N$ -particle system, respectively. In our case we are interested in obtaining the lowest IP as well as the lowest EA.

## Results and Discussions

We have used this above method to test the principle for H<sub>2</sub>O molecule. We started from the equilibrium geometry of H<sub>2</sub>O and stretched the O-H bonds symmetrically as well as asymmetrically. In another series of calculations we carried out symmetric as well as asymmetric distortions of H<sub>2</sub>O at a nonstable (linear) geometry. Computations were carried out by using the ACES program system,<sup>16</sup> using a double- $\zeta$  basis set plus a set of polarization functions on the oxygen and hydrogen atom.<sup>17</sup> This basis set, although not extensive, is good enough to test this principle. Most of the observations will remain valid even in an extended basis calculation. In Table I we have presented the ionization potentials, electron affinities, and consequent hardnesses and chemical potentials in Koopmans' approximation as well as the correlated MRCCSD approximation for the symmetric stretch of H<sub>2</sub>O. Table II reports the same numbers for the asymmetric stretch of H<sub>2</sub>O. Different trends are seen in these two tables. From Table I we see that the totally symmetric stretch gives a result in which there is no maximum or minimum in  $\mu$  or  $\eta$  near the equilibrium geometry. This applies to the symmetric distortion in bond lengths or bond angles. This has also been observed by PP<sup>4</sup> in their work. In fact  $\mu$  itself is not constant for the symmetric stretching and hence the principle cannot be tested in this case.

Some general observations are in order. The correlated values of  $\mu$  as well as  $\eta$  are significantly smaller than Koopmans' at each point of our calculation. The hardness values tend to decrease as bonds are stretched and the bond angles are increased and increase as the bonds are contracted and the bond angles are shortened. This trend remains the same with or without the correlation. Table II provides a case where the principle can be tested. We have provided results for the asymmetric distortion

TABLE III: Symmetric Distortion of Water Molecules at Linear Geometry<sup>a</sup>

O-H bond	$\eta_K$	$\mu_K$	$\eta_{Mrcc}$	$\mu_{Mrcc}$
+0.2 <sup>c</sup>	0.301 827	-0.155 032	0.256 114	-0.132 811
+0.1	0.319 853	-0.146 271	0.275 756	-0.125 231
+0.02	0.334 332	-0.139 567	0.291 582	-0.119 316
0.000 <sup>b</sup>	0.337 928	-0.137 960	0.295 524	-0.117 826
-0.02	0.341 506	-0.136 386	0.299 461	-0.116 433
-0.1	0.355 557	-0.130 508	0.315 887	-0.110 090
-0.2	0.372 204	-0.124 383	0.333 264	-0.105 433
HOH angle				
-5	0.338 222	-0.137 926	0.295 769	-0.117 807
-3	0.337 980	-0.137 952	0.295 603	-0.117 902
-1	0.337 945	-0.137 956	0.295 533	-0.117 869

<sup>a</sup> All values are in atomic units (au) except bond angles, which are in degrees. <sup>b</sup> Reference linear geometry when the O-H bond distance is 1.8091 au and the H-O-H bond angle is 180°. <sup>c</sup> (+) for stretching and (-) for contraction of the O-H bond.

TABLE IV: Asymmetric Distortion of Water Molecules at Linear Geometry<sup>a</sup>

O-H bond	$\eta_K$	$\mu_K$	$\eta_{Mrcc}$	$\mu_{Mrcc}$
0.2	0.329 739	-0.145 571	0.287 301	-0.125 010
0.08	0.336 513	-0.139 282	0.294 095	-0.119 125
0.04	0.337 570	-0.138 295	0.295 160	-0.118 191
0.000 <sup>b</sup>	0.337 928	-0.137 960	0.295 524	-0.117 826

<sup>a</sup> All values are in atomic unit (au). <sup>b</sup> Reference linear geometry when the O-H bond distance is taken to be 1.8091 au and the H-O-H bond angle is 180°.

of the H<sub>2</sub>O molecule. From symmetry arguments one can infer that at any level of calculation the values of IP, EA,  $\eta$ , and  $\mu$  for positive deviation will be the same as those for the negative deviation from equilibrium. For small asymmetric deviations around the equilibrium,  $\mu$  remains constant. We see that even at the correlated level of calculation, the hardness is maximum at equilibrium geometry. That this trend does not change from the Koopmans' calculation even after the inclusion of extensive correlation and relaxation is indeed gratifying. However, Table II again shows that the effects of correlation and relaxation tend to diminish the values of hardness and increase the values of chemical potential. In the case of the water molecule this seems so. Since  $\mu$  and  $\eta$  depend on IP and EA values, this aspect will be related to the relative values of relaxation and correlation in the  $(N-1)$  electron and  $(N+1)$  electron systems vis-à-vis the correlation of the ground  $N$ -electron system. As we see, at large distortions  $\mu$  changes quite significantly and hence the principle cannot be tested. But in the region where  $\mu$  and the external potential are constant,  $\eta$  is maximum at the symmetric equilibrium point.

A more useful and convincing test is provided by the distortion of H<sub>2</sub>O around nonstable geometries. This will allow us to compare symmetric stable geometry with symmetric nonstable cases. Tables III and IV report results for symmetric and asymmetric distortion of H<sub>2</sub>O at linear geometry, respectively. One can see that for symmetric distortions the trend of the results in Table III is similar to that of the Table I. The correlated values are considerably lower than Koopmans' values. However, since  $\mu$  is not constant, this does not provide a good test case. The hardness values tend to increase as bonds are contracted and decreases as bonds are stretched. In Table IV we have reported the asymmetric distortion around linear geometry. The hardness value is maximum at the symmetric point (with O-H bond distances the same as equilibrium geometry). The values are again less than Koopmans' values. However, if we compare the symmetric point of the linear H<sub>2</sub>O and the equilibrium point of the H<sub>2</sub>O (as in Table I or II), we find that  $\mu$  is nearly constant (varying in the fourth digit only), while  $\eta$  for the equilibrium point is more by 0.03 eV. We have computed  $\eta$  and  $\mu$  for other symmetric configurations with the H-O-H angle varying slightly

**TABLE V: Asymmetric Distortion of Ammonia Molecule<sup>a</sup>**

N-H bond	$\eta_K$	$\mu_K$	$\eta_{Mrec}$	$\mu_{Mrec}$
0.1	0.328 376	-0.089 581	0.289 582	-0.083 944
0.04	0.329 223	-0.088 717	0.290 303	-0.083 232
0.01	0.329 437	-0.088 532	0.290 523	-0.083 029
equil <sup>b</sup>	0.329 478	-0.088 508	0.290 693	-0.082 868
HNH angle				
8	0.327 609	-0.086 021	0.288 748	-0.080 639
5	0.328 379	-0.086 896	0.289 503	-0.081 455
3	0.328 844	-0.087 520	0.289 955	-0.082 045

<sup>a</sup> All values are in atomic units except bond angles, which are in degrees.<sup>b</sup> Equilibrium geometry in which the N-H bond distance = 1.91 au and the H-N-H bond angle is 106.7°.

from 180°. At all these points  $\eta$  is less than the corresponding equilibrium symmetric configuration value.  $\eta$  is maximum only at the equilibrium symmetric geometry (provided  $\mu$  is constant). Additionally, in Table III we find that a symmetric stretch of the O-H bond by 0.02 furnishes a  $\mu$  value that is almost the same as the equilibrium point in Table I or II but a substantially lower  $\eta$  value. Thus we see that at different geometries, as long as  $\mu$  is constant, the most stable point is provided by the one with maximum  $\eta$ .  $\eta$  is maximum at the equilibrium symmetric geometry (provided  $\mu$  is constant). This point is a convincing test of the principle of maximum hardness. The principle is quite far reaching in its utility, being only limited by the constraint of  $\mu$  and  $v$  being held constant. Additionally, we have presented the results for asymmetric distortion of a more complex example, ammonia. As observed by PP<sup>4</sup> and as seen in the case of H<sub>2</sub>O, a symmetric distortion will not lead to constant chemical potential. So we have presented results only for asymmetric distortion of ammonia in Table V. We observe that  $\mu$  is roughly constant and  $\eta$  is maximum at the equilibrium point. The trends are similar to those in Table II (for H<sub>2</sub>O).

It may be interesting if in the wavefunction formulation one can find a rigorous way of obtaining the derivatives of the  $E$  vs

$N$  plot more directly and thus provide a more direct test of this principle. Although the EA of H<sub>2</sub>O and NH<sub>3</sub> do not exist in a rigorous sense, the present approach, which computes  $\eta$  and  $\mu$  through eq 2, but at a near full CI level of accuracy, nevertheless, provides the most credible validation of this principle yet.

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