

Use of the chemical potential to improve energies from approximate wave functions

Ralph G. Pearson

Department of Chemistry, University of California, Santa Barbara, CA 93106, USA

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Summary. An equation derived from density functional theory is used to improve energies calculated from approximate wave functions. The examples used are perturbed particle in a box and harmonic oscillators. The equation depends on the constancy of the chemical potential in these systems. The results are quite promising.

Key words: Chemical potential – Density functional theory – Hardness – Local energy – Variance

1. Introduction

Recently a method was proposed for improving the energy of a trial density function [1]. The method is based on the properties of the electronic chemical potential, μ^0 , which must be constant everywhere in a chemical system [2]. It was shown that

$$\Delta E = \frac{-\langle(\mu - \mu^0)^2\rangle}{4\eta}, \quad (1)$$

where μ is the local chemical potential due to an approximate electron density, ρ , rather than the exact ρ^0 . The quantity η is the absolute hardness, defined as $2\eta = (\delta\mu/\delta\rho)_v$, where v is the potential due to the nuclei [3]. Similarly, $\mu^0 = (\delta E/\delta\rho)_v$.

While η is not constant, and can have local values, the quantity in (1) is the average, or global, value. It was assumed that $\eta = \langle t \rangle + \langle v_e \rangle$, the sum of the one-electron kinetic energy and the inter-electronic repulsion of two electrons in the same orbital. It is known that these are the terms which contribute to η [4]. The energy lowering of Eq. (1) results from electron density being transferred from regions where μ is too positive to regions where it is too negative. To be valid, the integrated amount of density transferred, ΔN , must be small. This means that the trial density, ρ , must be close to ρ^0 .

The working equation derived from Eq. (1) is

$$\Delta E = \frac{-\langle(\epsilon - \bar{\epsilon})^2\rangle}{4\eta} = \frac{-\delta^2}{4\eta}, \quad (2)$$

where ϵ is the local orbital energy [5] and $\bar{\epsilon}$ the average orbital energy. To be valid, $\bar{\epsilon}$ must be close to μ^0 . The variance is equal to δ , since $\langle(\epsilon - \bar{\epsilon})^2\rangle = \langle\epsilon^2\rangle - \langle\bar{\epsilon}\rangle^2$, and δ must be small.

The above concepts are usually applied to atoms and molecules, where the electrons are the quantized particles. However it is clear that the same ideas should apply to other cases, such as the particle in a box and the harmonic oscillator. This paper will deal with such systems. The goal is two-fold: to show that it is useful to define the chemical potential and hardness of such systems, and to see if Eq. (2) can be used to improve the energy of approximate wave functions for these cases.

Some change in terminology is appropriate. Thus μ^0 is simply the chemical potential and ϵ is the local energy of a single particle. The term chemical potential is appropriate, since in some cases μ^0 contributes directly to the thermodynamic quantity with that name, e.g. the vibration energy of molecules. In accordance with density functional theory, only ground states will be considered [6].

The examples used are particle in a box and harmonic oscillators with various perturbations. The unperturbed ground state wave functions are used for the approximate densities. In all cases the exact, or highly accurate, energy values can be found in the literature. Atomic units are used so that $m = e^2 = 1$, and $\hbar = 2\pi$.

2. A perturbed potential box

Consider a particle in a box with the potential equal to $-V_0$ for $l/2 > x > 0$ and $+V_0$ for $l > x > l/2$. The value of $\bar{\epsilon}$ will be $\pi^2/2l^2$ for the ground state, ϵ will be $\bar{\epsilon} \pm V_0$, and δ^2 will be simply V_0^2 . The value of η is the same as that of $\bar{\epsilon}$, so that the energy correction from Eq. (2) is

$$\Delta E = \frac{-V_0^2 l^2}{2\pi^2}. \quad (3)$$

To get an accurate energy, the second order perturbation energy is calculated by direct summation of the corrections for even values of n , up to $n = 10$ [7]. The result is $\Delta E = -0.467V_0^2 l^2/\pi^2$, very close to that in (3).

Further insight may be gained by looking at the changes in the particle density caused by the perturbation. Density should shift from the region of $+V_0$ to $-V_0$. The total amount transferred can be calculated from the equation [1]

$$|\Delta N| = \frac{\langle|\epsilon - \bar{\epsilon}|\rangle}{2\eta} = \frac{V_0 l^2}{\pi^2}. \quad (4)$$

The same calculation can be made from perturbation theory by adding in the appropriate bits of the excited state wave functions to the ground state, and squaring to get the correct density, ρ^0 .

$$|\Delta N| = \langle|\rho^0 - \rho|\rangle = 0.934V_0 l^2/\pi^2. \quad (5)$$

3. Perturbed harmonic oscillator

3.1. HO in a linear field

The potential energy is given by

$$V = \frac{1}{2}\omega^2 x^2 - Fx \quad (6)$$

with $\bar{\epsilon} = \omega/2$ and $\eta = \langle t \rangle = \omega/4$. The value of δ^2 is $\langle F^2 x^2 \rangle = F^2/2\omega$, so that $\Delta E = -F^2/2\omega^2$. The exact energy for the ground state is known to be $\omega/2 - F^2/F\omega^2$, so in this case the correction is exact [8].

The exact solution to (6) is that of a simple HO with the origin shifted from $x = 0$ to $x = F/\omega^2$. As expected, particle density is shifted in the direction where μ is more negative.

3.2. HO with a cubic potential

The potential energy is anharmonic,

$$V = \frac{1}{2}\omega^2 x^2 - Gx^3. \quad (7)$$

The values of $\bar{\epsilon}$ and η are the same as above, and $\delta^2 = \langle G^2 x^6 \rangle = 15G^2/8\omega^3$. The energy correction is $-15G^2/8\omega^2$. This is the same as an accurate value calculated by Herzberg using second-order perturbation theory [9].

3.3. HO with interaction term

The potential energy is given by

$$V = \frac{1}{2}\omega^2 x^2 + \frac{1}{2}\omega^2 y^2 + \alpha xy, \quad (8)$$

where α is small compared to ω^2 . We have $\epsilon = \omega$ and $\eta = \langle t_y \rangle + \langle t_x \rangle = \omega/2$. The value of δ^2 is $\langle \alpha^2 x^2 y^2 \rangle = \alpha^2/4\omega^2$, and the energy correction is $-\alpha^2/8\omega^3$. The exact energy for (8) is found by changing to the coordinates $(x + y)$ and $(x - y)$. The result is that

$$E = (\omega^2 + \alpha)^{1/2} + (\omega^2 - \alpha)^{1/2} = \omega \left(1 - \frac{\alpha^2}{8\omega^4} - \frac{15\alpha^4}{128\omega^8} \dots \right). \quad (9)$$

This agrees with the calculated value through the quadratic term.

A more complicated example is given by the Henon-Heiles potential [10].

$$V = \frac{1}{2}\omega_x^2 x^2 + \frac{1}{2}\omega_y^2 y^2 + \alpha y(x^2 + \beta y^2). \quad (10)$$

We have $\bar{\epsilon} = \omega_x/2 + \omega_y/2$ and

$$\delta^2 = \frac{3\alpha^2}{8\omega_x^2\omega_y} + \frac{3\alpha^2\beta}{4\omega_x\omega_y^2} + \frac{15\alpha^2\beta^2}{8\omega_y^3}. \quad (11)$$

There are two possible values of the hardness: $\eta = \omega_x/4 + \omega_y/4$, or $\eta = \omega_y/4$.

The exact energies are known for the potential (10), but only for definite values of ω_y , ω_x , α and β [10]. Taking the examples where $\omega_x = 1.3$ and $\omega_y = 0.7$, we can compare these values with those found from Eq. (2) with both choices for η . The uncorrected energy is $\epsilon = 1.0000$.

	$E(\omega_y)$	$E(\omega_x + \omega_y)$	E exact
$-\alpha = \beta = 0.1$	0.9930	0.9975	0.9955
$-\alpha = \beta = 0.2$	0.9559	0.9845	0.9621

It appears that better results are found if only t_y contributes to the hardness. This is sensible since ϵ changes markedly on going from $+y$ to $-y$, but is symmetric to $\pm x$. Thus it is the particle density with respect to the coordinate y which must change the most, and t_y will be the most affected. However, the calculations show some dependence on t_x .

4. Two mutually repelling HOs

An important example is provided by two isotropic harmonic oscillators which repel each other [11]. The potential function is

$$V = \frac{1}{2}\omega^2(r_1^2 + r_2^2) + \frac{\beta}{r_{12}}. \quad (12)$$

This provides a useful model for two electron systems, such as He, H^- and Li^+ with nuclear charge, Z . In the case of electrons where $\beta = e^2 = 1$, the energy in a.u. may be converted to HO units, $\omega/2$, by the relationship $\omega/2 = 8Z^2/9\pi$ a.u. This result comes from the properties of Gaussian orbitals [11].

The approximate wave function is the product of two three-dimensional HO functions, one for each electron. The uncorrected total energy is $6\omega/2 + \langle 1/r_{12} \rangle$. The last term can be evaluated easily by converting to center-of-mass and interparticle distance coordinates [11]. For the hydride ion, $Z = 1$, we find $\langle 1/r_{12} \rangle = 2.1213\omega/2$. Similarly $\delta^2 = \langle 1/r_{12}^2 \rangle - \langle 1/r_{12} \rangle^2$, is found to be $2.5688(\omega/2)^2$. The hardness is the single particle kinetic energy plus the interelectronic repulsion energy, $\eta = (1.5 + 2.1213)\omega/2$.

In this way total corrected energies can be calculated for H^- , He and Li^+ , as shown.

	E_{uncorr}	E_{corr}	E_{exact}
$Z = 1$	$8.1213\omega/2$	$7.9440\omega/2$	$7.8819\omega/2$
2	7.0607	6.9980	6.9980
3	6.7071	6.6748	6.6783

The exact values are those calculated by Kestner and Sinanoglu [11]. Notice that omission of the interelectronic repulsion in evaluating η , would lead to very poor results for the energy correction.

5. Conclusions

It appears that the concept of the chemical potential, μ , which is constant everywhere in a quantum system, is useful for particles other than electrons. The Eq. (2) for correcting the energy found from an approximate wave function, works very well for harmonic oscillators and particles in a box.

It is not clear why sometimes the correction gives exact answers, and sometimes not. The biggest uncertainty is in the value to use for the hardness, η .

It is clear that the kinetic energy and particle repulsion energies are the factors which contribute to η . However, it is very likely that the local hardness should enter in to the calculations, rather than the global value.

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