Remarks on Local Energy and Perturbations

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The local energy is first reviewed and compared with the expected energy. We then present the perturbative local energy method which uses an exactly soluble base problem and a perturbing potential to greatly simplify the expression of the local energy. This is demonstrated with two-electron atoms for which the method gives upper bounds with errors from 18% for He to 4% for Ne^{8+}. Finally a call to develop a local energy method for large systems is issued.

Key words: Local Energy; Variation Theorem; Perturbations.

1. Introduction

One way to approximate the ground-state eigenvalue for a given Hamiltonian, H, is to use the local energy. The local energy is defined quite differently from the expected energy, and it can provide both upper and lower bounds to the eigenvalue. The local energy is defined pointwise as

$$E[\psi, q] = \psi^{-1}(q)\, H\psi(q), \tag{1}$$

where q represents a set of coordinates. The local energy is obviously not defined at q if $\psi(q) = 0$. If $\psi(q)$ is an eigenfunction, then the local energy equals the eigenvalue except for the points (if any) where $\psi(q) = 0$. The points where $\psi(q) = 0$ are the nodes of the eigenfunction form a set of measure zero so that $E[\psi, q]$ is defined almost everywhere for an eigenfunction or any trial function that has realistic nodes (e.g. a trial function that is zero outside a certain radius does not have realistic nodes). The local energy is thus Lebesgue integrable. We now review the standard proof for the upper and lower bounds provided by the local energy [1].

We assume that $\psi_0(q)^* \psi(q)$ is everywhere positive except possibly on a set of measure zero where it is either positive or zero. Assume $H\psi_0 = E_0\psi_0$.

$$\begin{aligned} E_0 \int \psi_0^* \psi &= \int \psi_0^* H\psi = \int \psi_0^* \psi E[\psi, q] \\ &\le (\sup E[\psi, q]) \int \psi_0^* \psi, \end{aligned} \tag{2}$$

$$\begin{aligned} E_0 \int \psi_0^* \psi &= \int \psi_0^* H\psi = \int \psi_0^* \psi E[\psi, q] \\ &\ge (\inf E[\psi, q]) \int \psi_0^* \psi. \end{aligned} \tag{3}$$

The upper and lower bounds are then obtained by dividing by $\int \psi_0^* \psi$, which is positive. The supremum and infimum are over the set of coordinates q. This proof is quite elegant because it gives both the upper and lower bounds quite easily. The restriction on $\psi_0(q)^* \psi(q)$ is quite bothersome, however, and many applications have been restricted to ground states that are known to have no nodes since a trial function with no nodes is sufficient to satisfy the restriction on $\psi_0(q)^* \psi(q)$. If the ground state has nodes, then the trial function must also have nodes at the same places.

2. Comparison with the Variational Method

There is another proof for the upper bound, however, that avoids such restrictions and allows one to use very general functions for $\psi(q)$. Using normalized functions and the variational theorem we have

$$\begin{aligned} E_0 = \int \psi_0^* H\psi_0 \le \int \psi^* H\psi = \int \psi^* \psi E[\psi, q] \\ \le \sup E[\psi, q]. \end{aligned} \tag{4}$$

This proof allows more trial functions to be used and connects the supremum of the local energy to the energy expectation value. The result (4) has been given by Schmutz, although he forced the trial function to be positive [2]. Note that the energy expectation value is never inferior and thus would seem to provide the calculation of choice. For the energy expectation value, multidimensional integrals (usually at most two-electron integrals) are required. For the supremum of the local energy, one must search for the supremum of a multivariate function (usually over all the coordinates). To improve the energy bound for a trial function using either approach, variable parameters are added to the trial function. When the trial function is written as a linear combination of basis functions, the variable parameters are the coefficients of the basis functions, and the search for

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the lowest energy expectation value reduces to a simple matrix-eigenvalue problem – the linear variational method. Unfortunately, there is currently no simple algorithm to determine the trial function that gives the lowest supremum of the local energy, and thus the variational method is usually preferred. Nevertheless, very complex integrals may make the local energy method more attractive. Current work by Huang et al. for determining molecular energies and eigenfunctions uses powers of the Hamiltonian which generate very complex many-electron integrals which they calculate using Monte Carlo methods [3, 4].

For lower bounds to the energy there exists no simple theorem that complements the variational theorem for upper bounds. There are some lower bound techniques that resemble variational calculations, but they guarantee a lower bound to the ground-state energy only if *a priori* information is known about excited states [5–7]. Indeed, all current lower bound methods suffer from difficulties. Accurate lower bounds have been obtained only for systems of four particles or less [5–7]. Porras, et al., have very recently calculated lower bounds to the helium atom using the local energy and plan to extend their work to other two-electron atoms [8]. They address in detail the difficulties of searching for the infimum of the local energy and the restrictions placed on the trial functions.

3. The Perturbative Local Energy Method

It should be noted that the potential portion of the local energy is strikingly simple, having no dependence on the trial function:

$$E[\psi, q] = \psi^{-1}(q)\, H\psi\,(q) = \psi^{-1}(q)\,[T+V]\psi\,(q) = \psi^{-1}(q)\, T\psi\,(q) + V(q)\,, \tag{5}$$

where T and V are the kinetic and potential energy operators, respectively. One way to eliminate the more difficult kinetic portion is to separate the Hamiltonian $H = T + V$ into a base problem, $H_0 = T + V_0$, and perturbation, $P = V - V_0$. If a base problem eigenfunction ψ_0 and its energy E_0 are known and used to calculate the local energy of the perturbed Hamiltonian, then a very simple expression results:

$$E[\psi_0, q] = \psi_0^{-1}(q)\, H_0\psi_0(q) = \psi_0^{-1}(q)\,[H_0 + P]\psi_0(q) = E_0 + P(q)\,. \tag{6}$$

For N-electron atoms, one might think to choose the N-electron hydrogenic Hamiltonian as H_0 and the electron-electron repulsion potential as the perturbation P. Unfortunately, for this choice, the supremum of $P(q)$ is infinity and the infimum is zero, so that the upper bound to the atomic ground-state energy is infinity and the lower bound (provided $\psi_0^*\,\psi > 0$) is just the ground-state energy of the base problem. Obviously the base problem must be carefully chosen.

As an example, we consider two-electron atoms, defining $x = r_1$, $y = r_2$, and $z = r_{12}$, using the potentials

$$V_0(a,n) = -\frac{a}{x}\left(1+\frac{n}{2}\right) - \frac{a}{y}\left(1+\frac{n}{2}\right) + \frac{n(n+1)}{z^2} + \frac{an}{2z^2}\,\frac{(x-y)(x^2-y^2)}{xy}\,,$$
$$V = -\frac{Q}{x} - \frac{Q}{y} + \frac{1}{z}\,, \tag{7}$$

where Q is the nuclear charge. We define the base problem as $H_0(a, n) = T + V_0(a,n)$, the perturbation as $P(a,n) = V - V_0(a,n)$, and the perturbed Hamiltonian as $H = H_0(a,n) + P(a,n) = T + V$. An eigenfunction of the base problem is $\psi_0(a, n) = \exp(-a\,x)\exp(-a\,y)\,z^n$, with energy $E_0(a,n) = -a^2$ (the reader can check this by calculating $\psi_0^{-1} H_0\,\psi_0$). If we restrict to $a = 2Q/(n+2)$, then n is the only variable parameter and $P(n)$ is simpler since the Coulomb potentials for x and y in $V_0(n)$ and V cancel.

$$P(n) = \frac{1}{z} - \frac{n(n+1)}{z^2} - \frac{Qn}{(n+2)\,z^2}\,\frac{(x-y)(x^2-y^2)}{xy}\,. \tag{8}$$

We obtain an upper bound to $E[\psi_0, q]$ for the perturbed Hamiltonian as

$$E[\psi_0, q] = E_0 + \sup_{x,y,z} P(n) \le E_0 + \sup_z\left(\frac{1}{z} - \frac{n(n+1)}{z^2}\right) + \sup_{x,y,z} \frac{-Qn}{(n+2)\,z^2}\,\frac{(x-y)(x^2-y^2)}{xy}\,. \tag{9}$$

The supremum over x, y, and z on the right-hand-side of (9) is zero since $(x-y)(x^2-y^2)$ is always positive and equals zero for $x = y$. The supremum over z in (9) is $1/(4n(n+1))$. The resulting upper bound to the energy

$$E[\psi_0, q] \le -\left(\frac{2Q}{n+2}\right)^2 + \frac{1}{4n(n+1)} \tag{10}$$

can be minimized by varying n. The results are given in Table 1.

The success of this approach depends to a large extent on the base problem, and we are searching for better base problems and also other systems where this approach may be more advantageous.

As a final note, we remark that the Hartree-Fock method was a major achievement in early days of quantum chemistry in that it first made variational calculations on large systems possible. It did this by restricting the many-electron trial wavefunction to be formed from orthogonal one-electron orbitals. It would be interesting if a different type of restriction on the wavefunction could be found to reduce the labor of the multivariable extremum problem for the local energy method and make large systems computationally accessible by the energy method. The author feels that the search for such a restriction would be a very exciting and useful endeavor.

Table 1. We compare the ground-state energies of some two-electron atoms of charge Q [9] with the upper bounds derived in this paper (10). All units are in Hartree.

Q	– Energy	– Upper bound	Optimal n
2	2.90	2.38	0.300
3	7.28	6.40	0.189
4	13.7	12.4	0.137
5	22.0	20.4	0.108
6	32.4	30.4	0.0886
7	44.8	42.4	0.0753
8	59.2	56.4	0.0655
9	75.5	72.4	0.0579
10	93.9	90.4	0.0519

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