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Upper Bounds to the Overlap of Approximate and Exact Wavefunctions

M. G. Marmorino[1]

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One measure of how accurately an approximate wavefunction approximates the true wavefunction is the overlap of the two functions. In general the true wavefunction is not known so this overlap cannot be directly calculated. We derive two methods from the t expansion of Horn and Weinstein to bound from above the magnitude of the overlap of an approximate wavefunction with the ground state. The first method relies on the ability to divide the Hamiltonian into a base problem and a perturbation. The second method is more general and seems much more promising.

1. INTRODUCTION

If energy is the only criterion used to measure the accuracy of a wavefunction then one may use the variational theorem to assert that the wavefunction which gives the lowest energy is the best approximation to the ground-state. However, it is well known that energy-optimized wavefunctions need not predict the most accurate values for other observables. Another way to measure the accuracy of an approximate function is by its overlap with the true wavefunction—this is not biased towards any observable. An approximate normalized wavefunction, ψ, can be expanded in terms of the normalized eigenfunctions, ϕ_n, of the system's Hamiltonian:

$$\psi = \sum_{n=1}^{\infty} c_n \phi_n \tag{1}$$

where $c_n = \langle \psi | \phi_n \rangle$ and may be complex. The infinite sum of their square magnitudes, $|c_n|^2$, is unity. Since the true wavefunction is usually not known,

[1]Department of Chemistry, Faculty of Science, Ubon Ratchathani University, Warinchamrap, Ubon Ratchathani 34190, Thailand.

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this overlap can only be approximated or bounded. A lower bound to the magnitude of the overlap is easily derivable using the variational theorem (Christoffersen, 1989):

$$|c_1|^2 \geq \frac{E_2 - \langle H \rangle}{E_2 - E_1} \tag{2}$$

where E_1 and E_2 are the energies of the ground and first-excited states. An approximate lower bound, which is suspected to be very good if $|c_1|$ is high, is (Christoffersen, 1989):

$$|c_1| \geq 1 - \frac{\langle H \rangle - E_1}{2(E_2 - E_1)} \tag{3}$$

provided $\langle H \rangle \leq E_2$. Equation (3) is always higher than Eq. (2), but not necessarily better since it is approximate. Lower bounds to $|c_1|$ cannot achieve their full usefulness unless they are accompanied by an upper bound as well. For high values of $|c_1|$, unity can serve as an upper bound; however, for low values, unity does not provide for a tight bracketing of $|c_1|$. We now derive two different ways to get upper bounds to $|c_1|$.

2. THE *t* EXPANSION

The results in this paper rest on the *t* expansion (Horn and Weinstein, 1984). Letting H be the Hamiltonian operator and ψ be a trial function, they define a new normalized function parameterized by t:

$$\psi(t) = \frac{e^{-tH/2}\psi}{\langle \psi | e^{-tH} | \psi \rangle^{1/2}} \tag{4}$$

They state that $\psi(t)$ converges to the ground-state, ϕ_1, as t approaches infinity provided there is non-zero overlap of the ground state and the trial function. This can be seen if ψ is expanded in terms of the unknown eigenfunctions, ϕ_n, of H:

$$\psi(t) = \frac{e^{-Ht/2} \sum c_n \phi_n}{\langle \psi | e^{-Ht} | \psi \rangle^{1/2}} = \frac{\sum c_n e^{-E_n t/2} \phi_n}{\langle \psi | e^{-Ht} | \psi \rangle^{1/2}} \underset{t \to \infty}{\rightarrow} \phi_1 \tag{5}$$

As t increases, the low energy states have more weight compared to the high energy states until finally the ground state overwhelms all other states as t approaches infinity.

The energy can be written as a function of t, which is guaranteed to converge from above to the true ground-state energy as t approaches infinity.

$$E(t) = \langle\psi(t)|H|\psi(t)\rangle = \frac{\langle\psi|e^{-tH/2}He^{-tH/2}|\psi\rangle}{\langle\psi|e^{-tH}|\psi\rangle} \tag{6}$$

That $E(t)$ is a decreasing function can be shown by differentiating (6) with respect to t since $\langle H^2\rangle \geq \langle H\rangle^2$:

$$\frac{\partial E(t)}{\partial t} = \left(\frac{\langle e^{-tH/2}\psi|H|e^{-tH/2}\psi\rangle}{\langle e^{-tH/2}\psi|e^{-tH/2}\psi\rangle}\right)^2 - \frac{\langle e^{-tH/2}\psi|H^2|e^{-tH/2}\psi\rangle}{\langle e^{-tH/2}\psi|e^{-tH/2}\psi\rangle} < 0 \tag{7}$$

Horn and Weinstein presented the following equality for any operator A:

$$\frac{\langle e^{-tH/2}Ae^{-tH/2}\rangle}{\langle e^{-tH}\rangle} = \frac{\langle Ae^{-tH}\rangle}{\langle \mathrm{e}^{-tH}\rangle} \tag{8}$$

That (8) is incorrect in general can easily be shown using 2×2 matrices; however, we show this differently and obtain a useful result. Note that for $A = H$, however, (8) is true since H and e^{-tH} commute. We divide an arbitrary Hamiltonian, H, into a base problem, H_0, and a perturbation, P. We define ψ_0 and E_0 to be the base problem ground-state eigenfunction and eigenvalue, respectively. All expectation values are calculated with ψ_0. Using (8) with $A = H$ we have:

$$E(t) = \frac{\langle e^{-tH/2}H_0e^{-tH/2}\rangle}{\langle e^{-tH}\rangle} + \frac{\langle e^{-tH/2}Pe^{-tH/2}\rangle}{\langle e^{-tH}\rangle} = E_0 + \frac{\langle Pe^{-tH}\rangle}{\langle e^{-tH}\rangle} \tag{9}$$

We next use the variational principle in (9). If we assume that the ground state of the perturbed Hamiltonian is non-degenerate, then we have equality in (10) only if H and H_0 have the same ground state (this does not, however, imply that $H = H_0$, i.e., $P = 0$)

$$E_0 + \frac{\langle e^{-tH/2}Pe^{-tH/2}\rangle}{\langle e^{-tH}\rangle} \leq E_0 + \frac{\langle Pe^{-tH}\rangle}{\langle e^{-tH}\rangle} \tag{10}$$

This implies

$$P(t) = \frac{\langle e^{-tH/2}Pe^{-tH/2}\rangle}{\langle e^{-tH}\rangle} \leq \frac{\langle Pe^{-tH}\rangle}{\langle e^{-tH}\rangle} \tag{11}$$

where equality holds only if the perturbation does not disturb the ground state of the base problem. It seems that this inequality does not generalize for arbitrary functions or operators.

3. BOUNDS FOR BASE PROBLEM GROUND STATES

We again divide the Hamiltonian, H, into a base problem, H_0, and a perturbation, P. We further assume that the ground-state eigenvalue, E_0, and

normalized eigenfunction, ψ_0, of the base problem are known (knowledge of the full spectrum is not necessary).

We begin with the Cauchy–Schwarz inequality:

$$|\langle\psi_0|Pe^{-tH}|\psi_0\rangle| \leq \langle\psi_0|P^2|\psi_0\rangle^{1/2}\langle\psi_0|e^{-2tH}|\psi_0\rangle^{1/2} \tag{12}$$

We can then bound the magnitude of $P(t)$ using (12) in (11)

$$|P(t)| \leq \langle\psi_0|P^2|\psi_0\rangle^{1/2}\,\frac{\langle\psi_0|e^{-2tH}|\psi_0\rangle^{1/2}}{\langle\psi_0|e^{-tH}|\psi_0\rangle} \tag{13}$$

The ratio of exponential expectation values in Eq. (13) can be simplified by expanding ψ_0 in terms of the unknown normalized eigenfunctions, ϕ_n, of the perturbed Hamiltonian. As t approaches infinity, the first term in the summations of (14) dominates so that

$$\frac{\langle\psi_0|e^{-2tH}|\psi_0\rangle^{1/2}}{\langle\psi_0|e^{-tH}|\psi_0\rangle} = \frac{\left(\sum |c_n|^2 e^{-2tE_n}\right)^{1/2}}{\sum |c_n|^2 e^{-tE_n}} \underset{t\to\infty}{\to} \frac{1}{|c_1|} \tag{14}$$

We then have a bound on the magnitude of $P(t)$ in the limit of t approaching infinity, i.e., a bound on the magnitude of the ground-state expectation value $\langle P\rangle_{\text{gs}} = \langle\phi_1|P|\phi_1\rangle$.

$$|\langle P\rangle_{\text{gs}}| = \lim_{t\to\infty}|P(t)| \leq \frac{\langle\psi_0|P^2|\psi_0\rangle^{1/2}}{|c_1|} \tag{15}$$

If the observable of P is known (e.g., from experiment), then (15) can be used to bound $|c_1|$ for the ground state of any base problem.

The energy can also be used to derive bounds. Using the following expression for the ground-state energy of the perturbed Hamiltonian,

$$E(t) = \frac{\langle\psi_0|He^{-tH}|\psi_0\rangle}{\langle\psi_0|e^{-tH}|\psi_0\rangle} = E_0 + \frac{\langle\psi_0|Pe^{-tH}|\psi_0\rangle}{\langle\psi_0|e^{-tH}|\psi_0\rangle} \tag{16}$$

and (15) we have:

$$|E - E_0| \leq \frac{\langle\psi_0|P^2|\psi_0\rangle^{1/2}}{|c_1|} \tag{17}$$

which also gives an upper bound to $|c_1|$.

4. BOUNDS FOR ARBITRARY FUNCTIONS

In the following we work with only positive Hamiltonian operators. This is not a fundamental problem since the energy of every molecular system

can be bounded below by the united atom theorem (Thirring, 1978). Every atom can in turn be bounded below by summing the energy levels of the corresponding hydrogenic atom using the Pauli exclusion principle. The lower bound can then be subtracted from the molecular Hamiltonian to create a positive operator.

Given a trial function ψ we define $|c_1(t)| = |\langle\psi|\psi(t)\rangle|$ as an approximation to $|c_1| = |\langle\psi|\phi_1\rangle|$. As $\psi(t)$ approaches ϕ_1, $|c_1(t)|$ approaches $|c_1|$. That $|c_1(t)|$ decreases is shown by differentiation with respect to t and the monotonicity of $E(t)$:

$$2\langle e^{-tH}\rangle^{3/2}\frac{\partial|c_1(t)|}{\partial t} = \frac{\langle He^{-tH}\rangle}{\langle e^{-tH}\rangle} - \frac{\langle He^{-tH/2}\rangle}{\langle e^{-tH/2}\rangle} = E(t/2) - E(t/4) < 0 \quad (18)$$

Thus $|c_1(t)|$ bounds $|c_1|$ from above. We now derive an upper bound to $|c_1(t)|$. Expand the trial function ψ as a linear combination of the (we assume) complete set of unknown eigenfunctions, ϕ_n, of H (with corresponding eigenvalues E_n).

$$|c_1(t)| = \frac{\langle e^{-tH/2}\psi|\psi\rangle}{\langle e^{-tH/2}\psi|e^{-tH/2}\psi\rangle^{1/2}} = \frac{\sum_n |c_n|^2 e^{-tE_n/2}}{\left(\sum_n |c_n|^2 e^{-tE_n}\right)^{1/2}} \quad (19)$$

The numerator and denominator of (19) can be bounded from above and below using Taylor polynomials of different orders for e^{-x}: an even-order polynomial results in an upper bound to e^{-x} and an odd-order polynomial gives a lower bound. This is valid for $x \geq 0$, i.e., $tE_n \geq 0$. Since the Hamiltonian is assumed positive, E_n is always positive, so we must restrict $t \geq 0$. We form the following upper bounds $u(n, t)$ and lower bounds $l(n, t)$ to $|c_1(t)|$.

$$l(n,t) = \frac{\sum_{k=0}^{2n-1}(-t/2)^k\langle\psi|H^k|\psi\rangle/k!}{\left(\sum_{k=0}^{2n}(-t)^k\langle\psi|H^k|\psi\rangle/k!\right)^{1/2}} \leq |c_1(t)|$$

$$\leq \frac{\sum_{k=0}^{2n-2}(-t/2)^k\langle\psi|H^k|\psi\rangle/k!}{\left(\sum_{k=0}^{2n-1}(-t)^k\langle\psi|H^k|\psi\rangle/k!\right)^{1/2}} = u(n,t) \quad (20)$$

Since $|c_1(t)|$ is a decreasing function, the upper bound to $|c_1(t)|$ is also an upper bound to $|c_1|$. One must be careful with the upper bound, $u(n, t)$, since

the denominator will be non-positive for large t, thus destroying the bound due to division by zero or imaginary numbers. Note that $l(n, t)$ is a lower bound only to $|c_1(t)|$ and not $|c_1|$. To illustrate the bounds, Fig. 1 shows $l(n, t)$ and $u(n, t)$ compared with $|c_1(t)|$ for $n = 1$–8 for $\psi = 2^{-1/2}(\phi_1 + \phi_2)$ for a particle in a box of length π bohr. We define $t = T_n$ as the point past which $u(n, t)$ is no longer valid.

At this point we should point out that the trial function ψ is not entirely arbitrary; it must be carefully chosen to ensure that the expectation values of powers of the Hamiltonian exist (Huang, 2000; Marmorino, 2000). In addition, such integrals are much more difficult than the typical variational integrals, although this is not an insurmountable problem (Cioslowski, 1987; Huang, 1999; Huang, 2000).

5. CONCLUSION

We have introduced two methods to obtain upper bounds to the magnitude of the overlap of a trial function with the ground-state wavefunction. The first method relies on the ability to separate the Hamiltonian into a

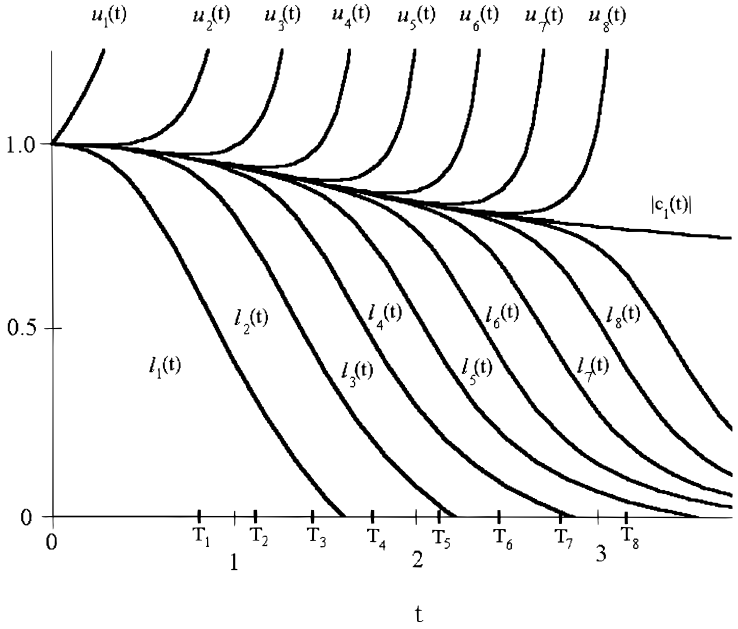

Fig. 1. Lower bounds $l(n, t)$ and upper bounds $u(n, t)$ to $|c_1(t)|$ for a particle-in-a-box wavefunction, ψ, are plotted. As n increases, the bounds better envelope the overlap of ψ with the ground state. $|c_1(t)|$ converges to $|c_1| = 2^{-1/2}$. Note that $u(n, t)$ gives upper bounds to $|c_1|$, but $l(n, t)$ does not give lower bounds to $|c_1|$.

base problem and a perturbation for which the ground-state eigenvalue and eigenfunction of the base problem are known. The resulting formulae require extra information, such as the ground-state expectation value of the pertrubation or the ground-state energy. The second method is suitable for almost any function and requires no extra information. The only difficulty lies in computing the expectation values of powers of the Hamiltonian.

Note added in proof: Equations (2–3) were first derived by Eckart [C. Eckart. The theory and calculation of screening constants. *Phys. Rev.* **36**, 878 (1930)]. To save space we avoided mentioning the extensive amount of previous work done in this area since our method is completely different, utilizing the *t*-expansion. Weinhold gave an excellent review of other methods many years ago. [F. Weinhold, Criteria of accuracy of approximate wavefunctions. *J. Math. Phys.* **11**, 2127 (1970)].

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