Engel 10.8

**Problem.** Follow the instructions provided to show that the energy of any model wave function $\Phi$ is greater than the true ground state energy (this is sometimes stated as, "the true ground state energy is a lower bound for the model energy").

**Answer.** Engel's instructions are straightforward (I hope). The following comments are designed to get you over any "sticky" points.

**a.** The energy associated with a model wave function is calculated using the same formula used to calculate the expectation value of the energy (this formula is given in Engel).

We get from the "expectation value" formula to the next formula by following these steps:

1. replace each $\Phi$ with $\sum_i c_i \psi_i$. Sticky point: Each time we make this replacement, we need to use a "fresh" index for the summation. There are four summations, so there should be four different indices. Engel shows only two indices which is not strictly correct.

2. after making the replacements, the summations are "inside" the integrals. The next step is to move the integral inside each pair of summations. Sticky point: every book that I have ever read has stated that "we assume that the integral and summations can be reordered as shown below...". I have no idea why they say this. To me it looks like a no-brainer, but there may be some situation where this re-ordering is not valid. If you're curious, go ask a mathematician. If you already know why, please come tell me.

**b.** The $\psi_i$ are eigenfunctions of the Hamiltonian and can be assumed to be orthogonal. Sticky point: if the eigenfunctions are degenerate, they need not be orthogonal, but we can always impose orthogonality by making a suitable choice of functions. Another sticky point: I will assume (like Engel) that all of the eigenfunctions have been normalized as well.

Since the eigenfunctions form an orthonormal set, all of the energy integrals simplify according to one of these two patterns:

\[ \int \psi_i \hat{H} \psi_i \, d\tau = \int \psi_i E_i \psi_i \, d\tau = E_i \int \psi_i \psi_i \, d\tau = E_i \]

\[ \int \psi_k \hat{H} \psi_i \, d\tau = \int \psi_k E_i \psi_i \, d\tau = E_i \int \psi_k \psi_i \, d\tau = 0 \]

Notice that the final equality on each line involves an overlap integral, and not an energy integral. The denominator contains overlap integrals and these are simplified using the orthonormality assumptions invoked above.

**c.** The formula for $E$ is a weighted average of $E_i$. Necessarily, $E$ is greater than the lowest $E_i$ because that is how averages work. Sticky point: prove that $E - E_0 > 0$. OK. I'll do it.

Starting with Engel's final formula

\[ E = \frac{\sum_n (c_n)^2 E_n}{\sum_n (c_n)^2} \]
Rearrange it and use the fact that $E_m > E_0$ to write an inequality

$$E \sum_m (c_m)^2 = \sum_m (c_m)^2 E = \sum_m (c_m)^2 E_m > \sum_m (c_m)^2 E_0$$

or pulling out two terms from above

$$\sum_m (c_m)^2 E > \sum_m (c_m)^2 E_0$$

which can be rearranged as shown below

$$\sum_m (c_m)^2 E - \sum_m (c_m)^2 E_0 > 0$$

$$\sum_m (c_m)^2 (E - E_0) > 0$$

$$(E - E_0) \sum_m (c_m)^2 > 0$$

A sum of squares is necessarily positive, so we can divide both sides of the inequality by this sum to obtain

$$E - E_0 > 0$$

Sticky point: At one point, I combined separate summations containing $E$ and $E_0$ into a single summation containing $(E - E_0)$. How do I know the same sequence of $c_m^2$ appear in both summations? Both sums were constructed from the same sequence of overlap integrals.