Chem 337, Fall 2018, Problems and **auxiliary problems, given in bold face**

problem_set_13

11/27/18  
Chpt 7: 7  

17. 

\[ |\psi> = c_a|a> + c_b|b> \]  

is a trail variational wavefunction for a diatomic molecule, where \(|a>\) is an atomic orbital centered on atom \(a\) and \(|b>\) is an atomic orbital centered on atom \(b\).

Given, \(<a|H|a> = \alpha_a, <b|H|b> = \alpha_b, <a|H|b> = \beta, <b|H|a> = \beta,\) and \(<a|b> = S,\) the “overlap”; with \(E = <\psi|H|\psi>/<\psi|\psi>,\) we showed in class that

\[ E = (c_a^2\alpha_a + c_b^2\alpha_b + 2c_ac_b\beta)/(c_a^2 + c_b^2 + 2c_ac_bS). \]  

Using \(\partial E/\partial c_a = 0,\) and \(\partial E/\partial c_b = 0\) to adjust \(c_a\) and \(c_b\) so as to minimize \(E,\) show that (as was asserted in class) these condition leads to the two equations 

\[ (\alpha_a - E) c_a + (\beta - ES) c_b = 0 \]  

\[ (\beta - ES) c_a + (\alpha_b - E) c_b = 0 \]  

which we then solved in class. Hint: “simplify” your equations obtained from \(\partial E/\partial c_a = 0,\) and \(\partial E/\partial c_b = 0\) by using (2) again.