

CHM 3411 - Physical Chemistry II
Chapter 10 - Supplementary Material

1. Approximation methods in quantum mechanics

Very few problems in quantum mechanics have exact solutions. Because of this, various methods for finding approximate solutions to a TISE have been developed. In many cases, the approximate solutions to a TISE are essentially exact – that is, they differ from the exact solutions by a negligible amount.

The two common methods for finding approximate solutions to a TISE are perturbation theory and variational theory. In many cases, an approach combining these two methods is used.

Perturbation theory.

Let H be the Hamiltonian for a TISE that cannot be solved exactly. We begin by breaking H into two parts – H_0 , which corresponds to a TISE that has an exact solution (or a high quality approximate solution), and H_1 , which includes the terms that make finding an exact solution to the TISE impossible. Since including H_1 changes the energies and wavefunctions found for the TISE for H_0 , H_1 is called a “perturbation”. The method for finding out how including H_1 affects the energies and wavefunctions is thus called perturbation theory.

For example, if we look at the TISE for the helium atom

$$H = -(\hbar^2/2m) \nabla_1^2 - (\hbar^2/2m) \nabla_2^2 - (Ze^2/4\pi\epsilon_0) (1/r_1) - (Ze^2/4\pi\epsilon_0) (1/r_2) + (e^2/4\pi\epsilon_0) (1/r_{12}) \quad (10.1.1)$$

we can divide the Hamiltonian into two parts

$$H_0 = -(\hbar^2/2m) \nabla_1^2 - (\hbar^2/2m) \nabla_2^2 - (Ze^2/4\pi\epsilon_0) (1/r_1) - (Ze^2/4\pi\epsilon_0) (1/r_2) \quad (10.1.2)$$

$$H_1 = (e^2/4\pi\epsilon_0) (1/r_{12}) \quad (10.1.3)$$

Since the Hamiltonian H_0 in eq 10.1.2 is separable, the TISE for H_0 can be solved exactly. We then try to determine how including H_1 affects the energies and wavefunctions found for the TISE for H_0 .

The usual way of proceeding is to write the Hamiltonian H in the following way

$$H = H_0 + \lambda H_1 \quad (10.1.4)$$

When $\lambda = 0$ we have $H = H_0$, corresponding to the TISE that we can solve. We then slowly allow λ to increase, and see how this affects the energies and wavefunctions for our system. When we reach $\lambda = 1$, we have the solutions for H , the Hamiltonian of interest.

There are general methods for finding the first order correction, the second order correction, and higher than second order corrections to the energy levels and wavefunctions, but we will not discuss this in detail. It is worth pointing out that perturbation theory was originally developed as a method in classical mechanics to describe the motion for a system of three (or more) particles interacting by gravitational attraction.

Variational theory.

The variational approach makes use of the variational theorem. Consider a TISE

$$H\Psi = E\Psi \quad (10.1.5)$$

whose solutions are not known. For simplicity, assume that the solutions are all singly degenerate (this assumption is not necessary but makes the derivation of the variational theorem a bit easier). Even though we do not know the

solutions to the TISE, we know they exist. Put the solutions ($\Psi_0, \Psi_1, \Psi_2, \dots$) in order from lowest energy to highest energy, so that ($E_0 < E_1 < E_2 < \dots$). Note that Ψ_0 is then the wavefunction for the ground state (state of lowest energy), and E_0 is the energy of the ground state.

Now consider some well-behaved normalized function f that is defined over the same region as our TISE. Because the solutions to a TISE form a complete, orthonormal set of functions, we can write f in terms of those functions

$$f = a_0\Psi_0 + a_1\Psi_1 + a_2\Psi_2 + \dots \quad (10.1.6)$$

where, since f is normalized, it follows

$$1 = |a_0|^2 + |a_1|^2 + |a_2|^2 + \dots \quad (10.1.7)$$

The average energy corresponding to a system whose state is given by f is then

$$E_f = \int f^* H f d\tau = \int (a_0\Psi_0 + a_1\Psi_1 + a_2\Psi_2 + \dots)^* H (a_0\Psi_0 + a_1\Psi_1 + a_2\Psi_2 + \dots) d\tau \quad (10.1.8)$$

Since $\Psi_0, \Psi_1, \Psi_2, \dots$ are eigenfunctions of H , we can rewrite eq 10.1.8 to get

$$E_f = \int (a_0\Psi_0 + a_1\Psi_1 + a_2\Psi_2 + \dots)^* (a_0E_0\Psi_0 + a_1E_1\Psi_1 + a_2E_2\Psi_2 + \dots) d\tau \quad (10.1.9)$$

Since the solutions to the TISE are orthonormal functions, then

$$\int \Psi_i^* \Psi_j d\tau = \delta_{ij} \quad \text{where } \delta_{ij} = 1 \text{ when } i = j, \delta_{ij} = 0 \text{ when } i \neq j \quad (10.1.10)$$

If we use eq 10.1.10 to evaluate the integrals in eq 10.1.9, the final result is

$$E_f = |a_0|^2 E_0 + |a_1|^2 E_1 + |a_2|^2 E_2 + \dots \quad (10.1.11)$$

or, subtracting E_0 from both sides of the equation

$$E_f - E_0 = |a_1|^2 (E_1 - E_0) + |a_2|^2 (E_2 - E_0) + \dots \quad (10.1.12)$$

Since every term on the right side of eq 10.1.12 has to be greater than or equal to zero, we have shown that

$$E_f - E_0 \geq 0 \quad (10.1.13)$$

or

$$E_f \geq E_0 \quad (10.1.13)$$

What does this mean? We have shown is that the value we calculate for E_f is an upper limit on the true value for the energy for the ground state. This is useful because if we modify our function f and get a lower value for E_f , we know that the modification has gotten us closer to the energy for the ground state.

Variational theory is based on the above result. We can write a function that has a number of terms that can be varied, and adjust each of those terms to minimize the value we calculate for E_f . The lower the value for E_f , the closer we are to the energy for the ground state. Note that nothing we have done requires that we actually know the location of the energy levels or wavefunctions for our system.

While the variational theorem applies only to the ground state of our system, it can be modified to find information about excited states and their energy. In any case, the ground state for a system is often the state we are most interested in. The variational theorem gives us a method that can be used to find better and better approximations for the ground state of a TISE.

2. Determination of electronic states (term symbols) for diatomic molecules

The electron configuration for the lowest energy state of a diatomic molecule may be found using the Pauli principle and aufbau principle in the same way as is done for atoms. Configurations for excited electronic states are also possible. Note that the ordering of molecular orbitals in terms of energy changes with the size of the system, with one ordering for molecules and ions up to and including N_2 and a slightly different ordering for O_2 , F_2 , Ne_2 , and their ions. For homonuclear diatomic molecules g/u symmetry (symmetry with respect to inversion through the center of mass of the molecule) applies to the individual molecular orbitals as well as the total wavefunction, with the σ bonding orbitals having g symmetry, the σ^* antibonding orbitals having u symmetry, the π bonding orbitals having u symmetry, and the π^* antibonding orbitals having g symmetry. These symmetry labels are not given in the figures in Atkins, but you are expected to know them and how they are determined. The Σ states of all diatomic molecules are also labeled as being either + or - symmetry (symmetry with respect to reflection of the wavefunction through a plane containing the molecular bond). You will not be expected to assign the +/- symmetry label, but will need to know the selection rule for +/- symmetry given below.

For a collection of N electrons in a diatomic molecule we may define an orbital angular momentum about the z-axis ($M_\Lambda \hbar$) and total spin angular momentum (S) in terms of the values for the individual electrons (λ, s). For a σ orbital the only possible value for λ is $\lambda = 0$. For a π orbital λ can be +1 or -1, and for a δ orbital λ can be +2 or -2. If we add the contributions from each electron, we get

$$M_\Lambda = \lambda_1 + \lambda_2 + \dots + \lambda_N \quad (10.2.1)$$

$$S = s_1 + s_2 + \dots + s_N \quad (10.2.2)$$

The only possible values for orbital angular momentum about the z-axis are $\pm \Lambda \hbar$. As before, values for M_S are found using

$$M_S = m_{s1} + m_{s2} + \dots + m_{sN} \quad (10.2.3)$$

The terms symbols corresponding to the different electronic states resulting from a particular electron configuration in a diatomic molecule are found by a procedure similar to that used for atoms.

- 1) Find all possible combinations of M_Λ and M_S for the electron configuration.
- 2) Find the largest value of M_Λ .
- 3) Find the largest value for M_S having the value of M_Λ found in step 2.
- 4) There will be one electronic state with a value of $|\Lambda|$ and S equal to the values of M_Λ and M_S found in steps 2 and 3 above. Eliminate one state for each possible combination of M_Λ and M_S corresponding to the value of $|\Lambda|$ and S you have found.
- 5) Go to step 2, and repeat this procedure until all of the electronic states have been found.

As a specific example of the above procedure consider the electronic states corresponding to the ground electronic configuration of the O_2 molecule. This electron configuration is $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(1\pi_u)^4(1\pi_g^*)^2$. Possible values for M_Λ and M_S are as follows:

$\lambda = +1$	$\lambda = -1$	M_Λ	M_S
$\uparrow \downarrow$		+2	0
\uparrow	\uparrow	0	+1
\uparrow	\downarrow	0	0
\downarrow	\uparrow	0	0
\downarrow	\downarrow	0	-1
	$\uparrow \downarrow$	-2	0

Based on the above table, there will be one state with $|\Lambda| = 2$ and $S = 0$. We eliminate two combinations from the above list for this state (+2,0) and (-2,0). There will now be a second state, with $|\Lambda| = 0$ and $S = 1$. We eliminate three combinations from the above list for this state (0,+1), (0,0), and (0,-1). This leaves one combination left, (0,0), which corresponds to a $|\Lambda| = 0$ and $S = 0$ state.

$ \Lambda $	S	term symbol
2	0	${}^1\Delta_g$
0	1	${}^3\Sigma_g^-$
0	0	${}^1\Sigma_g^-$

Hund's rules may be used to place these states in order of energy. In this case ${}^3\Sigma_g^- < {}^1\Delta_g < {}^1\Sigma_g^-$.

3. Selection rules for diatomic molecular electronic spectroscopy

The following selection rules apply for allowed transitions in diatomic molecules:

1) Orbital angular momentum selection rule. Note that $|\Lambda| = 0$ for a Σ state, $|\Lambda| = 1$ for a Π state, $|\Lambda| = 2$ for a Δ state, and so forth.

$$\Delta\Lambda = 0, \pm 1$$

2) Spin angular momentum selection rule

$$\Delta S = 0$$

3) g/u symmetry selection rule

allowed

forbidden

$g \rightarrow u$

$g \rightarrow g$

$u \rightarrow g$

$u \rightarrow u$

4) +/- selection rule (applies only to transitions between Σ states).

allowed

forbidden

$+\rightarrow +$

$+\rightarrow -$

$-\rightarrow -$

$-\rightarrow +$