Univeristy of Virginia: College of Arts and Sciences

CHEM 3410 Study Guide

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Disclaimer........................ 2 General Math 2

Course 1

Disclaimer

As a disclaimer, the following study guide is not intended to be comprehensive. Instead, I hope to offer an effective overview of the chapters deemed relevant to the course as far as I'm aware from *Physical Chemistry: A Molecular Approach* by Simon and McQuarrie. Please consult the textbook if you have any questions, comments, or concerns, and email me at mohan-shankar@virginia.edu if you think a change should be made.

Lastly, if something is referred to as Equation X or Figure Y, it should have an internal hyperlink to take you to the referenced item. With this in mind, I hope you find the following compendium of knowledge to be useful.

General Math

Complex Numbers

All numbers can be expressed as a combination of a real and imaginary part, making them complex. For example, the following is commonly seen

$$z = \underbrace{a}_{\text{Re}} + \underbrace{ib}_{\text{Im}} \tag{1.1.1}$$

where z is some complex number. The real part of z is given by a while the imaginary part is denoted by ib. Written more pretentiously, $\text{Re}\{z\} = a$ and $\text{Im}\{z\} = b$. If performing addition or subtraction, you add/sub real from real and imaginary from imaginary. Multiplication is done via FOIL and taking advantage of the fact that $i^2 = -1$. Division is aided by the introduction of the complex conjugate, an operation denoted by an asterisk.

$$z^* = a - bi \tag{1.1.2}$$

The magnitude of some complex number, z, is given by

$$|z| = \sqrt{|z|^2} \tag{1.1.3}$$

where

$$|z|^2 = z * z^* = (a + bi) * (a - bi) \tag{1.1.4}$$

It is important to remember that both Equation 1.1.3 and Equation 1.1.4 return real numbers.

Lastly, Euler's equation can be expressed as:

$$e^{i\alpha\theta} = cos(\alpha\theta) + isin(\alpha\theta) \tag{1.1.5}$$

where α is some arbitrary constant.

Operators & Eigenstuff

An operator is usually denoted as a capital letter with a hat. For example, the Hamiltonian, the energy operator, is denoted as follows: $\hat{H}$. An operator can include many operations including addition, multiplication, differentiation, integration, or a combination of them and many more. **Operators act on whatever functions lies to the right of them.**

The expectation value (think of this an the average) of an arbitrary operator can be denoted as follows:

$$< \hat{A} >= \int \psi(x)^* \hat{A} \psi(x) dx \tag{1.2.1}$$

Further, it is important to note that operators do not necessarily commute. That is to say

$$\int f(x)\hat{A}g(x)dx \neq \int g(x)\hat{A}f(x)dx$$

depending on the operator and the functions, f(x) and g(x). More generally, this can be taken to mean **order matters if non-commutative**.

As an example: take f(x) = g(x) = sin(x) here while $\hat{A} = x$, which is the position operator.

$$\int sin(x)xsin(x)dx = \int sin^2(x) * xdx$$

Because these two equations are equivalent, it is said that the operator commutes

If $\hat{A} = \frac{d}{dx}$

$$\int sin(x)\frac{d}{dx}sin(x)dx = \int sin(x)cos(x)dx \neq \int \frac{d}{dx}sin^2(x)dx$$

Since you can't rearrange the order of the functions and the operator, it can be said they do not commute

If an operator acting upon some function returns the same function with some scalar present, the function is considered to be an eigenfunction of the operator (here, "eigen" is German for "same"). Further, the scalar in front of the eigenfunction is referred to as the eigenvalue. Based on this definition, an eigenfunction is dependent on both the function and the operator.

$$\text{Ex. where } \hat{A} = \frac{d}{dx} \rightarrow \hat{A}[e^{\alpha x}] = \frac{d}{dx}[e^{\alpha x}] = \alpha e^{\alpha x}$$

Here, α is some constant, thus $e^{\alpha x}$ is an eigenfunction of the operator, $\frac{d}{dx}$ and α is the eigenvalue. Say we apply this same operator to a different function:

$$\hat{A}[x^2] = \frac{d}{dx}[x^2] = 2x$$

Since the function that was returned isn't some scaled quantity of x^2, that is to say αx^2, this polynomial is not an eigenfunction of the operator.

Operators have special types of properties. For example, they can be linear. This means that you can distribute the operator as if it were a constant. An example of a linear operator is the derivative:

$$\frac{d}{dx}[e^x + e^{2x}] = \frac{d}{dx}[e^x] + \frac{d}{dx}[e^{2x}]$$

An example of a non-linear operator would be to define some operator, $\hat{A}$ to take the reciprocal of whatever its input is.

$$\hat{A}[e^x] = 1/e^x = e^{-x}$$

If you tried to apply this to same system that differentiation was applied to above:

$$\hat{A}[e^x + e^{2x}] = \frac{1}{e^x + e^{2x}} \neq \hat{A}[e^x] + \hat{A}[e^{2x}] = \frac{1}{e^x} + \frac{1}{e^{2x}}$$

thus the operator is non-linear.

Another, special type of operators are called Hermitian. Their mathematical defintion is defined below:

$$\int \psi(x)^* \hat{A} \psi(x) dx = \int \psi(x) \hat{A} \psi(x)^* dx \tag{1.2.2}$$

This is taken to mean the complex conjugate and complex form commute with one another, also with respect to the operator. The eigenvalue of a hermitian operator corresponds to an observable quantity like energy, position momentum, etc. This is exemplified by the Schrodinger equation

$$\hat{H}\psi = E\psi \tag{1.2.3}$$

where the Hamiltonian ($\hat{H}$), the energy operator applied to the wavefunction (ψ) results in the energy of a specific level, E.

Even and Odd Functions

When integrating over all space

$$\int_{-\infty}^{+\infty} f(x)dx$$

it is useful to recall that odd functions are symmetric with respect to the origin. What this means for integration is that the positive and negative areas cancel out. Think of y = x as a general case. This does not hold true for even functions. Instead, they are symmetric about the y-axis which means you can halve your bounds of integration to $(2 * \int_{-\infty}^{0} f(x)dx)$ or $(2 * \int_{0}^{+\infty} f(x)dx)$ and evaluate from there which may be useful to get an actual answer.

Additionally, the following properties also hold true:

$$f(-x) = -f(x) \text{ if the function is odd}$$

$$f(-x) = f(x) \text{ if the function is even}$$

Lastly, it is important to remember even * odd = odd; even * even = even; odd * odd = even when dealing with functions.

Orthonormality

Orthonormality can be generally thought of as the integral of the function being evaluated to 0 or 1. It is generally expressed by the kroenecker delta

$$\delta_{n,m} \begin{cases} n = m, 1 \\ n \neq m, 0 \end{cases} \tag{1.3.1}$$

Ex.

$$\int \psi_n \psi_m dx = \delta_{n,m}$$

If $m \neq n$, the integral evaluates to 0
If $m = n$, the integral evaluates to 1

Orthogonal functions can be thought of as destructively interfering with one another like if you have two waves that are out of phase. To see this numerical result for yourself, type

$$\frac{1}{\pi} \int_{0}^{2\pi} sin(nx)sin(mx)$$

in Desmos. Set n and m to any integer value and check the result. It should be 0. Normalization means that there is a coefficient in front of the integral that makes the overall value 1 upon integration and application of the coefficient. In the same Desmos tab, make $n = m$ and the value you get should be one. This is because $1/\pi$ normalizes the result here. Without it, the integral would be π.

Lastly, I'll briefly explain how to find a normalization constant. Say we have some integral, I that is evaluated as follows:

$$I = \int_{\mathbb{R}} \psi(x)\psi^*(x)dx = c$$

where c $\neq$ 0 and $\mathbb{R}$ means bounds of $-\infty$ to $+\infty$. It's important to note that the bounds of the system may not always be $\mathbb{R}$. Instead, it could be $0 \longrightarrow L$, $0 \longrightarrow 2\pi$, $\{0 \longrightarrow \infty,\ 0 \longrightarrow 2\pi,\ 0 \longrightarrow \pi\}$, etc. To have this integral evaluate to 1, we divide I by c.

$$I = \frac{1}{C}\int_{\mathbb{R}} \psi(x)\psi^*(x)dx = 1$$

Since $\frac{1}{C}$ is a constant that we can remove from the integral, we can apply them to our wavefunction, ψ by doing $\psi = \sqrt{\frac{1}{c}} \cdot \psi$ since:

$$\sqrt{\frac{1}{c}}\psi \cdot \sqrt{\frac{1}{c}}\psi = \frac{1}{c}|\psi|^2$$

thus

$$\int_{\mathbb{R}} \sqrt{\frac{1}{c}}\psi(x)\sqrt{\frac{1}{c}}\psi(x)dx \longrightarrow \frac{1}{c}\int_{\mathbb{R}} \psi(x)\psi^*(x)dx = \frac{c}{c} = 1$$

Differential Equations

Many people often refer to differential equations as the language that the universe speaks in. Motion, population growth, and any phenomena dealing in change with respect to another variable(s) can be modeled using these equations. Further, it is important to note that solving these equations is contingent upon integration to go from the differential form to the "normal" function.

When solving these equations, there are a variety of techniques and patterns to be aware of, but for now, I will focus on one main one. It is important to recall that sin(x) and cos(x) are functions where, upon differentiating twice, return the same function with some coefficient in front.

$$\frac{d^2}{dx^2}[sin(\alpha x)] = -\alpha^2 sin(\alpha x)$$
$$\frac{d^2}{dx^2}[cos(\alpha x)] = -\alpha^2 cos(\alpha x)$$

Here, α is some constant. Perhaps the most useful function when solving differential equations is $e^{\alpha x}$ since its first derivative and all subsequent ones produce the same function with some coefficient in front.

$$\frac{d}{dx}[e^{\alpha x}] = \alpha e^{\alpha x} \rightarrow \frac{d^2}{dx^2}[e^{\alpha x}] = \alpha^2 e^{\alpha x}...$$

Given these properties, one should always consider $e^{\alpha x}$ if the differential equation has a second derivative present with a first derivative and/or the function itself. More rigorously, if the **operator** is any order derivative, $e^{\alpha x}$ is always an eigenfunction.

$$\text{Ex. } \frac{d^2y}{dx^2} - 3\frac{dy}{dx} + 2y = 0$$

Here, the second derivative is present with the first derivative and the function without differentiation. This signals that you should consider $e^{\alpha x}$ or some *linear combination* of exponential functions (a linear combination is just adding functions together with potentially different coefficients; an example being $c_1e^{\alpha x} + c_2e^{\alpha x}$). In this case, we will guess that the function, y = y(x) = f(x), has the form of $e^{\alpha x}$. That is to say,

$$y = f(x) = e^{\alpha x}$$

We must now find the value(s) of α, and this is done by substituting $y = e^{\alpha x}$

$$\frac{d^2}{dx^2}\left[e^{\alpha x}\right] - 3\frac{d}{dx}\left[e^{\alpha x}\right] + 2[e^{\alpha x}] = 0$$

$$\alpha^2 e^{\alpha x} - 3\alpha e^{\alpha x} + 2e^{\alpha x} = 0$$

$$\alpha^2 - 3\alpha + 2\left(e^{\alpha x}\right) = 0$$

$$\alpha^2 - 3\alpha + 2 = 0$$

We can now factor this equation and solve for the values of α that make this equation true

$$(\alpha - 2)(\alpha - 1) = 0 \rightarrow \alpha = 1\ ,\ \alpha = 2$$

Based off of this result, both e^x and e^{2x} satisfy the initial differential equation.

For $\alpha = 1$

$$\frac{d^2}{dx^2}\left[e^{x}\right] - 3\frac{d}{dx}\left[e^{x}\right] + 2[e^{x}] = 0$$

produces

$$e^x - 3e^x + 2e^x = 0$$

which is correct

For $\alpha = 2$

$$\frac{d^2}{dx^2}\left[e^{2x}\right] - 3\frac{d}{dx}\left[e^{2x}\right] + 2[e^{2x}] = 0$$

produces

$$(2^2)e^{2x} - 3 * 2e^{2x} + 2e^{2x} = 0$$

$$4e^{2x} - 6e^{2x} + 2e^{2x} = 0$$

which is also correct. Finally, it is important to recall that a derivative is a linear operator. That is to say it can be distributed:

$$\frac{d}{dx}[f(x) + g(x)] = \frac{d}{dx}[f(x)] + \frac{d}{dx}[g(x)] = \frac{df(x)}{dx} + \frac{dg(x)}{dx}$$

Leveraging this property, a linear combination of e^x and e^{2x} can be taken to make a general solution.

$$y = c_1e^x + c_2e^{2x}$$

Plugging this into the differential equation:

$$\frac{d^2}{dx^2}\left[c_1e^x + c_2e^{2x}\right] - 3\frac{d}{dx}\left[c_1e^x + c_2e^{2x}\right] + 2[c_1e^x + c_2e^{2x}] = 0$$

Using linearity to separate and factoring the constant terms out:

$$\left(c_1 \frac{d^2}{dx^2}\left[e^x\right] - 3c_1 \frac{d}{dx}\left[e^x\right] + 2c_1[e^x]\right) + \left(c_2 \frac{d^2}{dx^2}\left[e^{2x}\right] - 3c_2 \frac{d}{dx}\left[e^{2x}\right] + 2c_2[e^{2x}]\right) = 0$$

It was shown above that both sets of parentheses go to zero. The addition of the two constants make no difference since they will scale each term by the same amount. Writing this out explicitly:

$$\left(c_1 e^x - 3c_1 e^x + 2c_1 e^x\right) + \left(4c_2 e^{2x} - 6c_2 e^{2x} + 2c_2 e^{2x}\right) = 0$$