Problem Set 5 Answers
More Separation of Variables, Postulates 0-3

1. (a) $\mathcal{H}(x)\,\Psi(x) = E\,\Psi(x)$

$[-(\hbar^2/2m)\,d^2/dx^2 + \tfrac{1}{2}\,m\omega^2x^2\,]\,[2\omega m/h]^{1/4}\,\exp[-\pi\omega m x^2/h)]$

$= E[2\omega m/h]^{1/4}\,\exp[-\pi\omega m x^2/h]$

(b) To prove $\Psi(x)$ is an eigenfunction, substitute and see if it satisfies the equation.

$d/dx\,\exp[-\pi\omega m x^2/h] = -2(\pi\omega m/h)x\,\exp[-\pi\omega m x^2/h]$

$d^2/dx^2\,\exp[-\pi\omega m x^2/h] = -2(\pi\omega m/h)[1-(2x^2\pi\omega m/h)]\,\exp[-\pi\omega m x^2/h]$

$-(\hbar^2/2m)\{\,-(2\pi\omega m/h)[1-(2x^2\pi\omega m/h)]\,\exp[-\pi\omega m x^2/h]\}$

$+\tfrac{1}{2}\,m\omega^2x^2\,\exp[-\pi\omega m x^2/h)] = E?$

$-(\hbar^2/2m)\{\,-(2\pi\omega m/h)[1-(2x^2\pi\omega m/h)]\,\} + \tfrac{1}{2}\,m\omega^2x^2 = E?$

$-\tfrac{1}{2}\,m\omega^2x^2 + (\hbar^2/2m)(2\pi\omega m/h) + \tfrac{1}{2}\,m\omega^2x^2 = E?$

$\tfrac{1}{2}\,\hbar\omega = E$ Yes $\Psi(x)$ satisfies the equation and gives the eigenvalue.

(c) linear momentum operator is $(\hbar/i)d/dx$. The average value of linear momentum in this state is given by Postulate 3:

$\langle p_x\rangle = \int_{-\infty}^{\infty}\Psi(x)^*\,(\hbar/i)d/dx\Psi(x)dx$

$= (\hbar/i)\,[2\omega m/h]^{1/2}\int_{-\infty}^{\infty}\exp[-\pi\omega m x^2/h]\,d/dx\,\exp[-\pi\omega m x^2/h]dx$

is of the form $\int y\,dy$

$= -(\hbar/i)\,[2\omega m/h]^{1/2}\,\tfrac{1}{2}\,\mathbf{e}\mathrm{xp}[-2\pi\omega m x^2/h]|_{-\infty}^{\infty}$

$= 0$

(d) root mean square linear momentum $= \langle p_x^2\rangle^{1/2}$

the second deriv found already is $-(2\pi\omega m/h)[1-(2x^2\pi\omega m/h)]\,\exp[-\pi\omega m x^2/h]\}$

$\langle p_x^2\rangle = -\hbar^2\,[2\omega m/h]^{1/2}\int_{-\infty}^{\infty}\exp[-\pi\omega m x^2/h]d^2/dx^2\,\exp[-\pi\omega m x^2/h]dx$

$= -\hbar^2\,[2\omega m/h]^{1/2}\int_{-\infty}^{\infty}\exp[-\pi\omega m x^2/h]\bullet -2(\pi\omega m/h)[1-(2x^2\pi\omega m/h)]\,\exp[-\pi\omega m x^2/h]dx$

$= \hbar^2\,[2\omega m/h]^{1/2}\,(2\pi\omega m/h)\int_{-\infty}^{\infty}[1-(2x^2\pi\omega m/h)]\,\exp[-2\pi\omega m x^2/h]dx$

integrals are of the form $\int_0^{\infty}\exp(-a^2x^2)dx = (1/2a)(\pi)^{1/2}$ for $a > 0$

$\int_0^{\infty}x^2\,\exp(-ax^2)dx = (1/4a)(\,\pi/a)^{1/2}$ $a > 0$

first term in integral is $(1/2a)(\pi)^{1/2}$ where $a^2 = 2\pi\omega m/h$,

first term $= (h/8\omega m)^{1/2}$

second term in integral is $(-2\pi\omega m/h)\bullet\,(1/4a)(\,\pi/a)^{1/2}$ where $a = 2\pi\omega m/h$,

second term $= (-2\pi\omega m/h)\bullet h/8\pi\omega m\bullet(\,h/2\omega m)^{1/2} = -\tfrac{1}{2}(\,h/8\omega m)^{1/2}$

Since integrating from -∞ to ∞, multiply result of $\int_0^{\infty}$ by 2.

$\langle p_x^2\rangle = \hbar^2\,[2\omega m/h]^{1/2}\,(2\pi\omega m/h)\bullet(\,h/8\omega m)^{1/2} = \hbar\,(\omega m)/2$

$= \hbar\omega m/2$

root mean square $= \langle p_x^2\rangle^{1/2} = [\hbar\omega m/2]^{1/2}$

(e) Probability of finding the particle within an infinitesimal distance dx of the position x = $(h/\pi\omega m)^{1/2}$ is given by $\Psi^*\Psi$

$\Psi^*\Psi = [2\omega m/h]^{1/2} \exp[-2\pi\omega m x^2/h]$.

For $x = (h/\pi\omega m)^{1/2}$ value is $[2\omega m/h]^{1/2} \exp[-2\pi\omega m/h\ (h/\pi\omega m)] = [2\omega m/h]^{1/2} \exp[-2]$

(f) Average position of the particle is

$\langle x\rangle = \int_{-\infty}^{\infty} \Psi(x)^*\, x\Psi(x)dx = [2\omega m/h]^{1/2} \int_{-\infty}^{\infty} x\exp[-2\pi\omega m x^2/h]dx = ?$

This integral is of the form $\int_{-\infty}^{\infty} y\,dy$

$\langle x\rangle = 0$ because $\exp[-\infty]$ at both limits.

(g) Root mean square position is $\langle x^2\rangle^{1/2}$

$\langle x^2\rangle = \int_{-\infty}^{\infty} \Psi(x)^*\, x^2\Psi(x)dx = [2\omega m/h]^{1/2} \int_{-\infty}^{\infty} x^2\exp[-2\pi\omega m x^2/h]dx$

This integral is of the form $\int_0^{\infty} x^2 \exp(-ax^2)dx = (1/4a)(\pi/a)^{1/2}$ where $a = 2\pi\omega m/h$, multiply by 2 since integral is from $-\infty$ to $+\infty$.

$\langle x^2\rangle = h/4\pi\omega m = \hbar/2\omega m$

$\langle x^2\rangle^{1/2} = [\hbar/2\omega m]^{1/2}$

(h) Product of $\langle x^2\rangle^{1/2}\langle p_x^2\rangle^{1/2}$ is $[\hbar/2\omega m]^{1/2}[\hbar\omega m/2]^{1/2} = \hbar/2$

(i) Diatomic molecule has mean displacement $\langle(R-R_{eq})\rangle = \langle x\rangle = 0$ in this state. Mean square displacement is $\langle(R-R_{eq})^2\rangle = \hbar/2\omega m$

When m is increased to M, mean displacement is still 0, mean square displacement = $\hbar/2\omega M$, decreases. Heavier isotopes have smaller mean square displacement, smaller amplitudes of vibration than lighter isotopes.

2. (a) Schrodinger eq is

$$\{ -(\hbar^2/2m)[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2] + \tfrac{1}{2}[\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2] \}\Psi(x,y,z) = E\,\Psi(x,y,z)$$

where $\kappa_x = m\omega_x^2$, $\kappa_y = m\omega_y^2$, $\kappa_z = m\omega_z^2$.

(b) How you would find the eigenfunctions and eigenvalues of this physical system; use separation of variables:

Let $\Psi(x,y,z) = P(x)\bullet Q(y)\bullet R(z)$, substitute it into the Schr. equation:

$$\{ -(\hbar^2/2m)[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2] + \tfrac{1}{2}[\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2] \} P(x)\bullet Q(y)\bullet R(z) = E\, P(x)\bullet Q(y)\bullet R(z)$$

Then divide both sides of the equation by $P(x)\bullet Q(y)\bullet R(z)$ to get

$$\frac{[-(\hbar^2/2m)\partial^2/\partial x^2 + \tfrac{1}{2}\kappa_x x^2]\,P(x)}{P(x)} + \frac{[-(\hbar^2/2m)\partial^2/\partial y^2 + \tfrac{1}{2}\kappa_y y^2]\,Q(y)}{Q(y)} + \frac{[-(\hbar^2/2m)\partial^2/\partial z^2 + \tfrac{1}{2}\kappa_z z^2]\,R(z)}{R(z)} = E$$

Since each term involves only x or only y or only z, then each must be equal to a constant and the sum of the constants must equl the eigenvalue E

Therefore we find that we have to solve 3 equations, one in x, one in y, one in z.

$$[-(\hbar^2/2m)\partial^2/\partial x^2 + \tfrac{1}{2}\kappa_x x^2]\,P(x) = e\,P(x)$$

and the others look just like this except in the variables y and z.
We already have the eigenfunctions and eigenvalues of the x equation:
$\varphi(x)$ and energies are $(n + \tfrac{1}{2})\hbar\omega$
Since the y and z equations are analogous then we know those eigenfuncitons and energies as well. We need the x, y, z subscripts to identify the various quantum numbers and harmonic frequencies which are different from each other (since $\kappa_x \neq \kappa_y \neq \kappa_z$) :

$E = (n_x + \tfrac{1}{2})\hbar\omega_x + (n_y + \tfrac{1}{2})\hbar\omega_y + (n_z + \tfrac{1}{2})\hbar\omega_z$

$\Psi(x,y,z) = \varphi(x)\bullet\varphi(y)\bullet\varphi(z)$

The eigenvalue for the ground state of the three-dimensional anisotropic harmonic oscillator.

$E = (n_x + \tfrac{1}{2})\hbar\omega_x + (n_y + \tfrac{1}{2})\hbar\omega_y + (n_z + \tfrac{1}{2})\hbar\omega_z$ are the general eigenvalues of this system where $n_x = 0,1,2,3,4 \ldots$ $n_y = 0,1,2,3,4 \ldots$ $n_z = 0,1,2,3,4 \ldots$

Ground state $E = (0+\tfrac{1}{2})\hbar\omega_x + (0+\tfrac{1}{2})\hbar\omega_y + (0+\tfrac{1}{2})\hbar\omega_z$

The eigenfunction of the ground state of the three-dimensional anisotropic harmonic oscillator.

$$\Psi(x,y,z) = \varphi(x)\bullet\varphi(y)\bullet\varphi(z)$$

$$= [2\omega_x m/h]^{1/4}\exp[-\omega_x m x^2/2\hbar]\bullet[2\omega_y m/h]^{1/4}\exp[-\omega_y m y^2/2\hbar]$$

$$\bullet\,[2\omega_z m/h]^{1/4}\exp[-\omega_z m z^2/2\hbar]$$

3. Since in the imaginary universe the gravitational terms exactly opposite and equal to the e-e repulsion, then

(a) $\mathcal{H} = -(\hbar^2/2M_n)\nabla_n^2 - (\hbar^2/2m_e)\{\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \ldots\} - Ze^2/r_1 - Ze^2/r_2 - Ze^2/r_3 - Ze^2/r_4 \ldots$

$\mathcal{H} = -(\hbar^2/2\mu)\{\nabla_1^2 + \nabla_2^2 + \nabla_3^2 + \nabla_4^2 + \ldots\} - Ze^2/r_1 - Ze^2/r_2 - Ze^2/r_3 - Ze^2/r_4 \ldots$

$\mathcal{H}\,\Psi(1, 2, 3, 4,\ldots) = E\,\Psi(1, 2, 3, 4,\ldots)$ can be solved by solving individual *one-electron problems*:

$$\{-(\hbar^2/2\mu)\nabla_i^2 + V(r_i)\}\psi(r_i, \theta_i, \phi_i) = E_i\,\psi(r_i, \theta_i, \phi_i.)$$

(b) For He atom in this universe,

$$\{-(\hbar^2/2\mu)\{\nabla_1^2 + \nabla_2^2\} - Ze^2/r_1 - Ze^2/r_2\}\Psi(1, 2) = E\,\Psi(1, 2)$$

(c) Eigenfunctions are $\Psi(1, 2) = \psi(r_1,\theta_1,\phi_1)\bullet\psi(r_2,\theta_2,\phi_2)$

where $\psi(r_1,\theta_1,\phi_1) = R_{nl}(r_1)\Theta_{lm}(\theta_1)\Phi(\phi_1)$ in which the functions are the hydrogen functions with Z=2. The eigenvalues are the hydrogen atom eigenvalues, $-Z^2/n^2\bullet e^2/2a_0$

(d) Energy level diagram for He atom (not to scale)

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----------------- 2s 4s, 2s4p, 2s4d, 2s4f $-2^2(2^{-2}+4^{-2})\ e^2/2a_0 = -1.25\ e^2/2a_0$
----------------- 2s3s, 2s3p, 2s3d $-2^2(2^{-2}+3^{-2})\ e^2/2a_0 = -1.44...\ e^2/2a_0$

----------------- $2s^2$ $-2^2(2^{-2}+2^{-2})\ e^2/2a_0 = -2\ e^2/2a_0$

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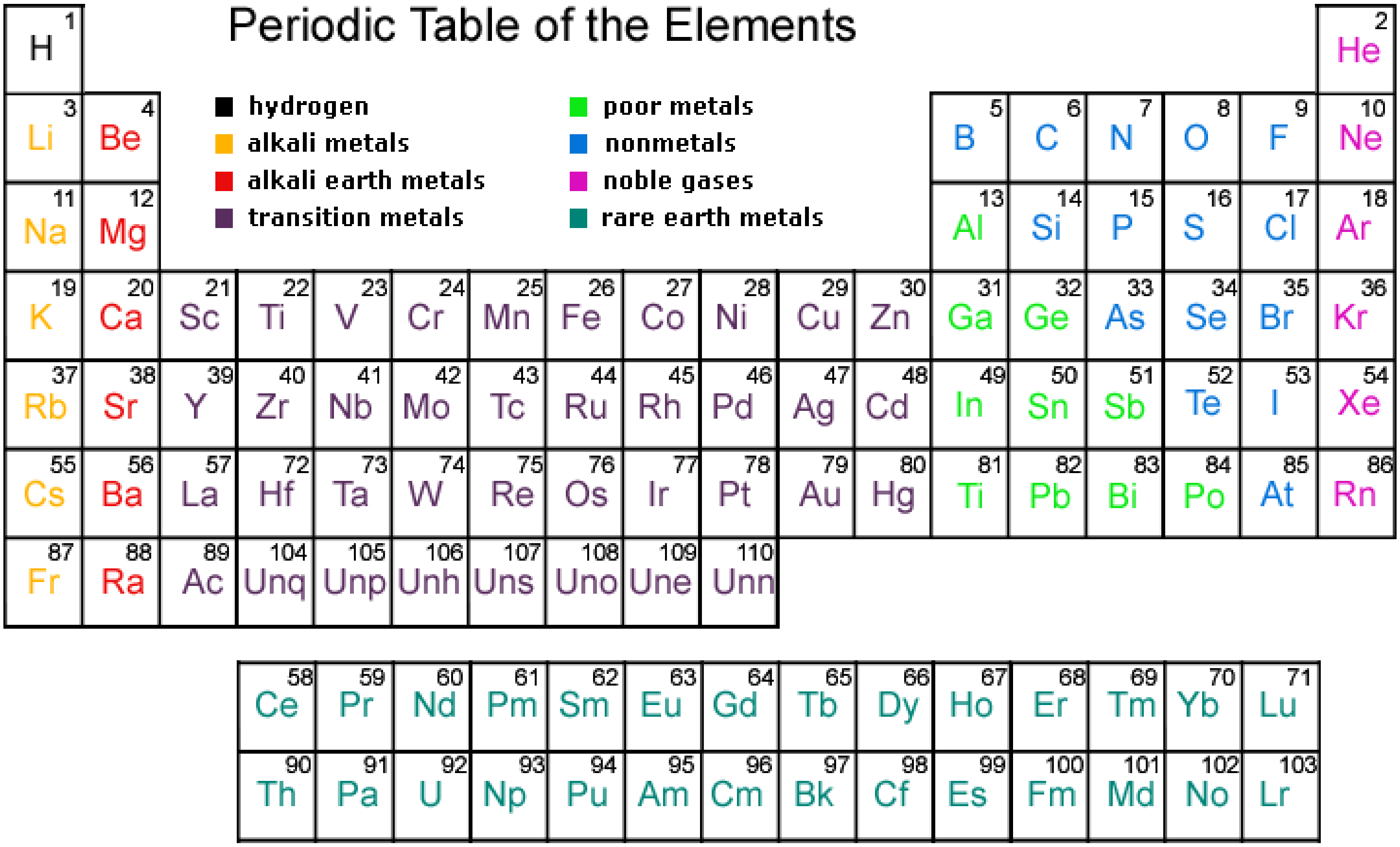
----------------- 1s 4s, 1s4p, 1s4d, 1s4f $-2^2(1^{-2}+4^{-2})\ e^2/2a_0 = -4.25\ e^2/2a_0$
----------------- 1s3s, 1s3p, 1s3d $-2^2(1^{-2}+3^{-2})\ e^2/2a_0 = -4.44...\ e^2/2a_0$

----------------- 1s2s, 1s2p $-2^2(1^{-2}+2^{-2})\ e^2/2a_0 = -5\ e^2/2a_0$

----------------- $1s^2$ $-2^2(1^{-2}+1^{-2})\ e^2/2a_0 = -8\ e^2/2a_0$

(e) Ground state energy = $[-Z^2/1^2 - Z^2/1^2]\bullet e^2/2a_0 = -8\ e^2/2a_0$ This is much lower energy than that of He atom in our universe, $-2.904\ e^2/2a_0$ because the repulsion between the two electrons has been nullified by the gravitational term in the imaginary universe.

(f) Atomic structure in this universe is predictable entirely from hydrogen atom states. Energy level diagrams will be given entirely by a sum of $-Z^2\{\Sigma_i(1/n_i^2)\}\ \bullet e^2/2a_0$ where the n_i quantum numbers are assigned according to Pauli principle. Since there is no “screening”, every electron sees the full charge of the nucleus. Because of this, the ground state energies will be much lower, the <u>atomic radii will be much smaller</u>, the <u>ionization energies will be greater</u> than in our universe. Because the relationship between the quantum numbers n, ℓ, m_ℓ , s and m_s are the same as in our universe, the Periodic Table for the first 2 rows will be the same, as the filling H 1s; He $1s^2$; Li $1s^22s$ degenerate with $1s^22p$; Be $1s^22s^2$ degenerate with $1s^22s2p, 1s^22p^2$; B $1s^22s^22p$ degenerate with $1s^22s2p^2$, $1s^22p^3$; C $1s^22s^22p^2$, degenerate with $1s^22s2p^3$, $1s^22p^4$; N $1s^22s^22p^3$, degenerate with $1s^22s2p^4$, $1s^22p^5$; O $1s^22s^22p^4$, degenerate with $1s^22s2p^4$, $1s^22p^5$, F $1s^22s^22p^5$, Ne $1s^22s^22p^6$, Na $1s^22s^22p^63s$, degenerate with $1s^22s^22p^63p$, $1s^22s^22p^63d$; Mg $1s^22s^22p^63s^2$, degenerate with, among others, $1s^22s^22p^63p^2$, $1s^22s^22p^63d^2$; and so on. Note that Li and Na will have a valence electron that is in the next higher n than the core, just as in our universe. Similarly Mg will have 2 valence electrons that are in the next higher n than the core. Al $1s^22s^22p^63s^23p$, degenerate with, among others, $1s^22s^22p^63d^3$; Si $1s^22s^22p^63s^23p^2$, degenerate with, among others, $1s^22s^22p^63d^4$. Since C and Si will have 4 valence electrons that are in the next higher n than the core, they will have similar properties that arise from this. Thus, periodicity in properties will be preserved in the imaginary universe, however, after the first two rows, the positions of the elements in the Periodic Table of the imaginary universe will be different from ours. The inert gases will be different. Ne is a closed shell, but the next closed shell is not Ar $1s^22s^22p^63s^23p^6$ degenerate with, among others, $1s^22s^22p^63d^8$, instead it will be Z= 28 or Ni $1s^22s^22p^63s^23p^63d^{10}$. And then the next closed shell will be Z= 60 or Nd $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}$. There would be no transition element series, because the d and f subshells will be degenerate with the s and p subshells for the same n. Compare with ours below: The imaginary universe will have a Periodic Table but different from ours starting from the 3rd row.



Periodic Table of the Elements

■ hydrogen
■ alkali metals
■ alkali earth metals
■ transition metals
■ poor metals
■ nonmetals
■ noble gases
■ rare earth metals

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Ti	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

As we have seen above, because of the degeneracies which remain in the various subshells due to lack of screening in the imaginary universe, the closed shells come with Z=2, 10, 18, 60, ..., so besides atomic radii being much smaller and ionization energies much larger, the periodicity in the atomic radii and in the ionization potentials will be very different from ours.