hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 * *	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

*Lanthanide series	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
* *Actinide series	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Key integrals and identities:

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \sin\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx$$

$$\left(\frac{a}{2}\right)\delta_{mn} = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\cos\left(\frac{m\pi x}{a}\right)dx$$

$$0 = \int_0^a \cos\left(\frac{n\pi x}{a}\right)\sin\left(\frac{m\pi x}{a}\right)dx$$

$$\frac{a^2}{4} = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 x dx$$

$$\left(\frac{a}{2\pi n}\right)^3\left(\frac{4\pi^3 n^3}{3} - 2\pi n\right) = \int_0^a \left(\sin\left(\frac{n\pi x}{a}\right)\right)^2 x^2 dx$$

$$\frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \int_0^\infty e^{-\alpha x^2} dx$$

$$\left(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\right)\left(\frac{(2n-1)(2n-3)\cdots(3)(1)}{(2\alpha)^n}\right) = \int_0^\infty x^{2n} e^{-\alpha x^2} dx \qquad n = 1, 2, 3, \ldots$$

$$\left(\frac{1}{2}\right)\left(\frac{n!}{\alpha^{n+1}}\right) = \int_0^\infty x^{2n+1} e^{-\alpha x^2} dx \qquad n = 0, 1, 2, \ldots$$

$$2\sin(x)\sin(y) = \cos(x-y) - \cos(x+y) \quad \rightarrow \quad 2\sin^2 x = 1 - \cos(2x)$$

$$2\cos(x)\cos(y) = \cos(x-y) + \cos(x+y) \quad \rightarrow \quad 2\cos^2 x = 1 + \cos(2x)$$

$$.\ 2\sin(x)\cos(y) = \sin(\alpha+\beta) + \sin(\alpha-\beta) \quad \rightarrow \quad 2\sin x\cos x = \sin(2x) \quad .$$

$$\sin(x+y) = \sin x\cos y + \cos x\sin y \quad \rightarrow \quad \sin(2x) = 2\sin x\cos x$$

$$\cos(x+y) = \cos x\cos y - \sin x\sin y \quad \rightarrow \quad \cos(2x) = \cos^2 x - \sin^2 x$$

Paul

VALUES OF SOME PHYSICAL CONSTANTS

Constant	*Symbol*	*Value*
Avogadro's number	N_0	$6.02205 \times 10^{23}\ \mathrm{mol^{-1}}$
Proton charge	e	$1.60219 \times 10^{-19}\ \mathrm{C}$
Planck's constant	h $\hbar$	$6.62618 \times 10^{-34}\ \mathrm{J \cdot s}$ $1.05459 \times 10^{-34}\ \mathrm{J \cdot s}$
Speed of light in vacuum	c	$2.997925 \times 10^{8}\ \mathrm{m \cdot s^{-1}}$
Atomic mass unit	amu	$1.66056 \times 10^{-27}\ \mathrm{kg}$
Electron rest mass	m_e	$9.10953 \times 10^{-31}\ \mathrm{kg}$
Proton rest mass	m_p	$1.67265 \times 10^{-27}\ \mathrm{kg}$
Boltzmann constant	k_B	$1.38066 \times 10^{-23}\ \mathrm{J \cdot K^{-1}}$ $0.69509\ \mathrm{cm^{-1}}$
Molar gas constant	R	$8.31441\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Permittivity of a vacuum	ε_0 $4\pi\varepsilon_0$	$8.854188 \times 10^{-12}\ \mathrm{C^2 \cdot s^2 \cdot kg^{-1} \cdot m^{-3}}$ $1.112650 \times 10^{-10}\ \mathrm{C^2 \cdot s^2 \cdot kg^{-1} \cdot m^{-3}}$
Rydberg constant (infinite nuclear mass)	R_∞	$2.179914 \times 10^{-23}\ \mathrm{J}$ $1.097373\ \mathrm{cm^{-1}}$
First Bohr radius	a_0	$5.29177 \times 10^{-11}\ \mathrm{m}$
Bohr magneton	μ_B	$9.27409 \times 10^{-24}\ \mathrm{J \cdot T^{-1}}$
Stefan-Boltzmann constant	σ	$5.67032 \times 10^{-8}\ \mathrm{J \cdot m^{-2} \cdot K^{-4} \cdot s^{-1}}$

CONVERSION FACTORS FOR ENERGY UNITS

	joule	*kJ·mol⁻¹*	*eV*	*au*	*cm⁻¹*	*Hz*
1 joule $=1$		6.022×10^{20}	6.242×10^{18}	2.2939×10^{17}	5.035×10^{22}	1.509×10^{33}
1 kJ·mol⁻¹ $= 1.661 \times 10^{-21}$		1	1.036×10^{-2}	3.089×10^{-4}	83.60	2.506×10^{12}
1 eV $= 1.602 \times 10^{-19}$		96.48	1	3.675×10^{-2}	8065	2.418×10^{14}
1 au $= 4.359 \times 10^{-18}$		2625	27.21	1	2.195×10^{5}	6.580×10^{15}
1 cm⁻¹ $= 1.986 \times 10^{-23}$		1.196×10^{-2}	1.240×10^{-4}	4.556×10^{-6}	1	2.998×10^{10}
1 Hz $= 6.626 \times 10^{-34}$		3.990×10^{-13}	4.136×10^{-15}	1.520×10^{-16}	3.336×10^{-11}	1

SOME MATHEMATICAL FORMULAS

$$\sin\alpha\sin\beta = \tfrac{1}{2}\cos(\alpha-\beta) - \tfrac{1}{2}\cos(\alpha+\beta)$$
$$\cos\alpha\cos\beta = \tfrac{1}{2}\cos(\alpha-\beta) + \tfrac{1}{2}\cos(\alpha+\beta)$$
$$\sin\alpha\cos\beta = \tfrac{1}{2}\sin(\alpha+\beta) + \tfrac{1}{2}\sin(\alpha-\beta)$$
$$\sin(\alpha\pm\beta) = \sin\alpha\cos\beta \pm \cos\alpha\sin\beta$$
$$\cos(\alpha\pm\beta) = \cos\alpha\cos\beta \mp \sin\alpha\sin\beta$$
$$e^{\pm i\theta} = \cos\theta \pm i\sin\theta$$
$$\cos\theta = \frac{e^{i\theta}+e^{-i\theta}}{2}$$
$$\sin\theta = \frac{e^{i\theta}-e^{-i\theta}}{2i}$$
$$f(x) = f(a) + f'(a)(x-a) + \frac{1}{2!}f''(a)(x-a)^2 + \frac{1}{3!}f'''(a)(x-a)^3 + \cdots$$
$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \cdots$$
$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \cdots$$
$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \cdots$$
$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \cdots \qquad x^2 < 1$$
$$(1\pm x)^n = 1 \pm nx \pm \frac{n(n-1)}{2!}x^2 \pm \frac{n(n-1)(n-2)}{3!}x^3 \pm \cdots \qquad x^2 <$$
$$\int_0^\infty x^n e^{-ax}\,dx = \frac{n!}{a^{n+1}} \qquad (n \text{ positive integer})$$
$$\int_0^\infty e^{-ax^2}\,dx = \left(\frac{\pi}{4a}\right)^{1/2}$$
$$\int_0^\infty x^{2n}e^{-ax^2}\,dx = \frac{1\cdot3\cdot5\cdot\cdots\cdot(2n-1)}{2^{n+1}a^n}\left(\frac{\pi}{a}\right)^{1/2} \qquad (n \text{ positive integer})$$
$$\int_0^\infty x^{2n+1}e^{-ax^2}\,dx = \frac{n!}{2a^{n+1}} \qquad (n \text{ positive integer})$$
$$\int_0^a \sin\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = \int_0^a \cos\frac{n\pi x}{a}\cos\frac{m\pi x}{a}\,dx = \frac{a}{2}\delta_{nm}$$
$$\int_0^a \cos\frac{n\pi x}{a}\sin\frac{m\pi x}{a}\,dx = 0 \qquad (m \text{ and } n \text{ integers})$$

<u>Short Answer Questions:</u>
The following text refers to problems 1-8.

Among the many possible wavefunctions associated with the $^7\mathrm{G}$ term symbol, suppose you are given the one with the largest possible values for the J quantum number (total angular momentum) and the M_J quantum number (total angular momentum about the z-axis). This wavefunction is denoted $\Psi^{^7\mathrm{G}}_{J^{(\max)}M_J^{(\max)}}$.

1. What is the degeneracy of an atomic state described by the $^7\mathrm{G}$ term symbol?

2-3. What are the maximum values for the total angular momentum and the total angular momentum around the *z*-axis.

________ $J^{(\max)}$

________ $M_J^{(\max)}$

3-8. What are the eigenvalues of $\hat{L}^2, \hat{J}^2, \hat{S}^2, \hat{L}_z, \hat{S}_z, \hat{J}_z$. Be sure to show the dependence on $\hbar$.

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9. Write the key equation known as "Fermi's Golden Rule."

10. Write a Slater determinant of molecular orbitals that is appropriate for the *ground* state of the Lithium Hydride cation, LiH^+. Label the molecular orbitals with symmetry labels, i.e. $\sigma_u, \sigma_g, \pi_u^+, \pi_u^-, \pi_g^+, \pi_g^-, \ldots$. <u>Use the long form of the Slater determinant, writing out all the rows and columns.</u>

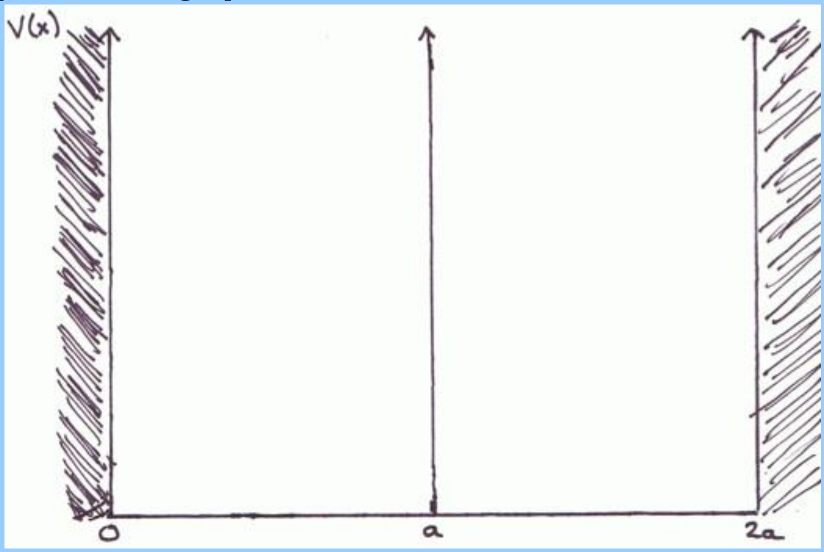
11. Because of the presence of other electrons and the positive nuclei, electrons in large molecules and solids do not experience the full Coulomb potential. Instead, they experience a screened Coulomb potential. (You learned about this in thermodynamics, as it is a key component of the Debye-Hückel theory of electrolyte solutions.) A common model for the screened Coulomb potential is the Yukawa potential,

$$V_{\mathrm{Y}}(r) = \frac{q_1 q_2 e^{-\lambda r}}{4\pi\varepsilon_0 r}$$

where r is the separation between the particles. **Write the Hamiltonian for two particles, with charges q_1 and q_2 and masses m_1 and m_2 whose interaction is described by the Yukawa potential.**

The following text refers to problems 12-15.
Consider an electron confined to two one-dimensional boxes with infinitely repulsive sides. The two boxes are adjacent to each other but separated by an infinite barrier, as shown in the following figure and encapsulated by the following equation:

$$V(x) = \begin{cases} +\infty & x \le 0 \\ 0 & 0 < x < a \\ +\infty & x = a \\ 0 & a < x < 2a \\ +\infty & x \ge 2a \end{cases}$$



12. The system is prepared in its ground state and then its absorption spectrum is taken. The largest-wavelength absorption that is observed has wavelength 1000 nm. **How wide are the boxes? (I.e., what is the value of a?)**

13. **What is the ground state energy of this system?**

14,15. An experiment reveals that the system has a 90% chance of being observed in the first box and a 10% chance of being observed in the second box. **Write <u>TWO</u> wavefunctions, which differ from each other by more than a constant factor, that are consistent with this observation.**

Part 2. Problems

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1. Properties of the Second Derivative Operator.
In this problem, you will derive some properties of the second derivative operator,

$$\left\langle \Psi(x) \left| \frac{d^2}{dx^2} \right| \Psi(x) \right\rangle$$

1a. Explicitly show that the second derivative operator is Hermitian. [6 points]

1b. Explicitly show that the second derivative operator is negative semidefinite. That is, show that for <u>any</u> wavefunction, $\Psi(x)$,

$$\left\langle \Psi(x) \left| \frac{d^2}{dx^2} \right| \Psi(x) \right\rangle \le 0 .$$

[4 points]

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2. Atomic Diffraction and Neutron Diffraction.
Suppose we use a beam of Helium-4 atoms to image a crystal, in a manner similar to *X*-ray crystallography. Assume that the ${}_2^4\mathrm{He}$ atoms are in thermal equilibrium at temperature *T*. From fundamental thermodynamics, we know that the kinetic energy of the Helium atoms is

$$\text{kinetic energy} = \tfrac{3}{2} k_B T \qquad (1)$$

where k_B is Boltzmann's constant. Suppose that the substance we want to diffract the Helium atoms from crystallizes in a simple cubic lattice with lattice constant (i.e., nearest-neighbor distance) $a = 3.0 \cdot 10^{-10}$ m.

2a. At what temperature would diffraction of the ${}_2^4\mathrm{He}$ atoms become appreciable? (6 points)

2b. Suppose we use thermal neutrons, instead of ${}_2^4\mathrm{He}$ to diffract off the crystal. **Would the optimal temperature of the neutrons be smaller or larger than that of the Helium atoms in part (a)? (2 points)**

(i) $T_{\text{neutrons}} > T_{\text{Helium}}$ (ii) $T_{\text{neutrons}} < T_{\text{Helium}}$

2c. Suppose we now decide to diffract ${}_2^4\mathrm{He}$ from a cubic lattice with a slightly smaller lattice constant, $a = 2.8 \cdot 10^{-10}$ m. **Should the temperature of the Helium atom beam be increased or decreased in order to optimize diffraction. (2 points)**

(i) $T_{\text{He for .28 nm}} > T_{\text{He for .20 nm}}$ (increase T) (ii) $T_{\text{He for .28 nm}} < T_{\text{He for .20 nm}}$ (decrease T)

3. Mathematical results related to infinitesimal unitary transformations.

Let $\hat{C}(\boldsymbol{\tau})$ be a time-independent Hermitian operator. Let $\Psi_k(\boldsymbol{\tau})$ denote the eigenfunctions of the Hamiltonian, $\hat{H}(\boldsymbol{\tau})$. Denote the ground-state wavefunction as $\Psi_0(\boldsymbol{\tau})$.

3a. Show that for any eigenfunction of the Hamiltonian, the following expectation value is zero:

$$\left\langle \Psi_k \middle| \left[\hat{H}, \hat{C} \right] \middle| \Psi_k \right\rangle = 0$$

(3 points)

3b. Show that the expectation value of the following double-commutator is always greater than or equal to zero for the ground-state wavefunction,

$$\left\langle \Psi_0 \middle| \left[\hat{C}, \left[\hat{H}, \hat{C} \right] \right] \middle| \Psi_0 \right\rangle \geq 0$$

(7 points)