QM3 workshop 3, Problem 1: The Hermitian operator A has eigenvectors u, v, $A\,u = \lambda\,u$, $A\,v = \mu\,v$. A commutes with the Hermitian operator B, $[A, B] = 0$. (a) Show that if $\lambda \neq \mu$ then u, v are also eigenvectors of B. (b) When there is double degeneracy, i.e. $\lambda = \mu$, explain where the proof fails and sketch how we can obtain two eigenvectors of B. (Not full derivation.)

Problem 2 Two non-interacting electrons, bound by the attractive potential $v(\boldsymbol{r})$, are described by the 2-electron Slater determinant Φ:

$$\Phi(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_2, \sigma_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(\boldsymbol{r}_1)\,\chi_1(1) & \psi_1(\boldsymbol{r}_2)\,\chi_1(2) \\ \psi_2(\boldsymbol{r}_1)\,\chi_2(1) & \psi_2(\boldsymbol{r}_2)\,\chi_2(2) \end{vmatrix}$$

The non-interacting Hamiltonian that describes the system is:

$$H_0 = h(\boldsymbol{r}_1, \boldsymbol{p}_1) + h(\boldsymbol{r}_2, \boldsymbol{p}_2), \qquad h(\boldsymbol{r}, \boldsymbol{p}) = -\frac{\hbar^2 \nabla^2}{2m} + v(\boldsymbol{r})$$

- Show that the expectation value of H_0 is

$$\langle \Phi | H_0 | \Phi \rangle = \sum_{i=1}^{2} \int d^3r\, \psi_i^*(\boldsymbol{r}) \Big(-\frac{\hbar^2}{2m}\, \nabla^2 \psi_i(\boldsymbol{r}) \Big) + \int d^3r\, \rho(\boldsymbol{r})\, v(\boldsymbol{r}), \qquad \rho(\boldsymbol{r}) = \sum_{i=1}^{2} |\psi_i(\boldsymbol{r})|^2$$

[Hint: work out first $\langle \Phi | h | \Phi \rangle = \iint d^3r_1\, d^3r_2\, \Phi^*(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_2, \sigma_2)\, h(\boldsymbol{r}_1, \boldsymbol{p}_1)\, \Phi(\boldsymbol{r}_1, \sigma_1; \boldsymbol{r}_2, \sigma_2)$]

Problem 3: Localised identical particles can be considered as distinguishable

Two identical particles are localised in positions A and B and do not interact. We ignore spin. The (normalised) wave-function that describes one of the particles localised at A is $\phi_A(\boldsymbol{r})$ and the (normalised) wave-function that describes one of the particles localised at B is $\phi_B(\boldsymbol{r})$. The wave-functions $\phi_A(\boldsymbol{r})$, $\phi_B(\boldsymbol{r})$ do not overlap anywhere in space: $\phi_A(\boldsymbol{r})\,\phi_B(\boldsymbol{r}) = 0$, $\forall\ \boldsymbol{r}$.

Indistinguishable particles must be described with a wave-function of the correct symmetry. For two bosons/fermions, the two-particle wave-function is

$$\Psi_{AB}^{\text{ind}}(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{\sqrt{2}} \left[\phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}') \pm \phi_B(\boldsymbol{r})\, \phi_A(\boldsymbol{r}') \right]$$

Distinguishable particles are described with a simple product wave-function:

$$\Psi_{AB}^{\text{dis}}(\boldsymbol{r}, \boldsymbol{r}') = \phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}')$$

a. Are these two-particle wave functions normalised?

b. Work out the expression for the expectation values of the operator $\hat{O}_1 = O_1(\boldsymbol{r}, \boldsymbol{p}) + O_1(\boldsymbol{r}', \boldsymbol{p}')$:

$$\langle \Psi_{AB}^{\text{ind}} | \hat{O}_1 | \Psi_{AB}^{\text{ind}} \rangle = \frac{1}{2} \iint d^3r\, d^3r'\ \left[\phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}') \pm \phi_B(\boldsymbol{r})\, \phi_A(\boldsymbol{r}') \right]^* \left[O_1(\boldsymbol{r}, \boldsymbol{p}) + O_1(\boldsymbol{r}', \boldsymbol{p}') \right] \left[\phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}') \pm \phi_B(\boldsymbol{r})\, \phi_A(\boldsymbol{r}') \right]$$

$$\langle \Psi_{AB}^{\text{dis}} | \hat{O}_1 | \Psi_{AB}^{\text{dis}} \rangle = \iint d^3r\, d^3r'\, \phi_A^*(\boldsymbol{r})\, \phi_B^*(\boldsymbol{r}') [O_1(\boldsymbol{r}, \boldsymbol{p}) + O_1(\boldsymbol{r}', \boldsymbol{p}')] \phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}')$$

c. Work out the expression for the expectation values of the operator $\hat{O}_2 = O_2(|\boldsymbol{r} - \boldsymbol{r}'|)$:

$$\langle \Psi_{AB}^{\text{ind}} | \hat{O}_2 | \Psi_{AB}^{\text{ind}} \rangle = \frac{1}{2} \iint d^3r\, d^3r'\ \left[\phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}') \pm \phi_B(\boldsymbol{r})\, \phi_A(\boldsymbol{r}') \right]^* O_2(|\boldsymbol{r} - \boldsymbol{r}'|) \left[\phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}') \pm \phi_B(\boldsymbol{r})\, \phi_A(\boldsymbol{r}') \right]$$

$$\langle \Psi_{AB}^{\text{dis}} | \hat{O}_2 | \Psi_{AB}^{\text{dis}} \rangle = \iint d^3r\, d^3r'\, \phi_A^*(\boldsymbol{r})\, \phi_B^*(\boldsymbol{r}') O_2(|\boldsymbol{r} - \boldsymbol{r}'|) \phi_A(\boldsymbol{r})\, \phi_B(\boldsymbol{r}')$$

What is your conclusion?

Problem 4: Why we need approximations in theory of electronic structure.

This problem is to demonstrate that the amount of information in the many-particle wavefunction $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ is overwhelming and that it is hopeless to attempt to solve Schrödinger's equation numerically, fully, i.e. without introducing some approximation. Below we ignore spin.

(a) Estimate the amount of information in the wavefunction $\psi(\boldsymbol{r})$ for the electron in the H atom, when we know the values of this function on a grid inside a box. Use a coarse grid with 10 grid points per coordinate x, y, z. How much capacity (in bytes) would it take to store this wf in memory? (A real number requires 4 bytes).

(b) Repeat the estimate for the wf of the Li atom. Does the amount of information in the wf for one state of the Li atom fit in a DVD? A DVD holds $\sim$ 10GB.

(c) For the atom of which element would the mass of DVDs required to store the wf of a single state exceed (i) the mass of the Earth? (ii) the mass of the Sun? (iii) the mass of the Milky Way? (DVD mass $\sim$ 1g, Earth mass $\sim 6 \times 10^{24}$ kg, solar mass $\sim 2 \times 10^{30}$kg, mass of Milky Way $\sim 5 \times 10^{11}$ solar masses.)

Table of elements.pdf

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.933	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.732	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.922	34 **Se** Selenium 78.09	35 **Br** Bromine 79.904	36 **Kr** Krypton 84.80
37 **Rb** Rubidium 84.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molibdenum 95.94	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.327	57-71 Lanthanides	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.967	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103 Actinides	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [268]	110 **Ds** Darmstadtium [269]	111 **Rg** Roentgenium [272]	112 **Cn** Copernicium [277]	113 **Uut** Ununtrium unknown	114 **Fl** Flerovium [289]	115 **Uup** Ununpentium unknown	116 **Lv** Livermorium [298]	117 **Uus** Ununseptium unknown	118 **Uuo** Ununoctium unknown

57 **La** Lanthanum 138.906	58 **Ce** Cerium 140.115	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.24	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.966	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]