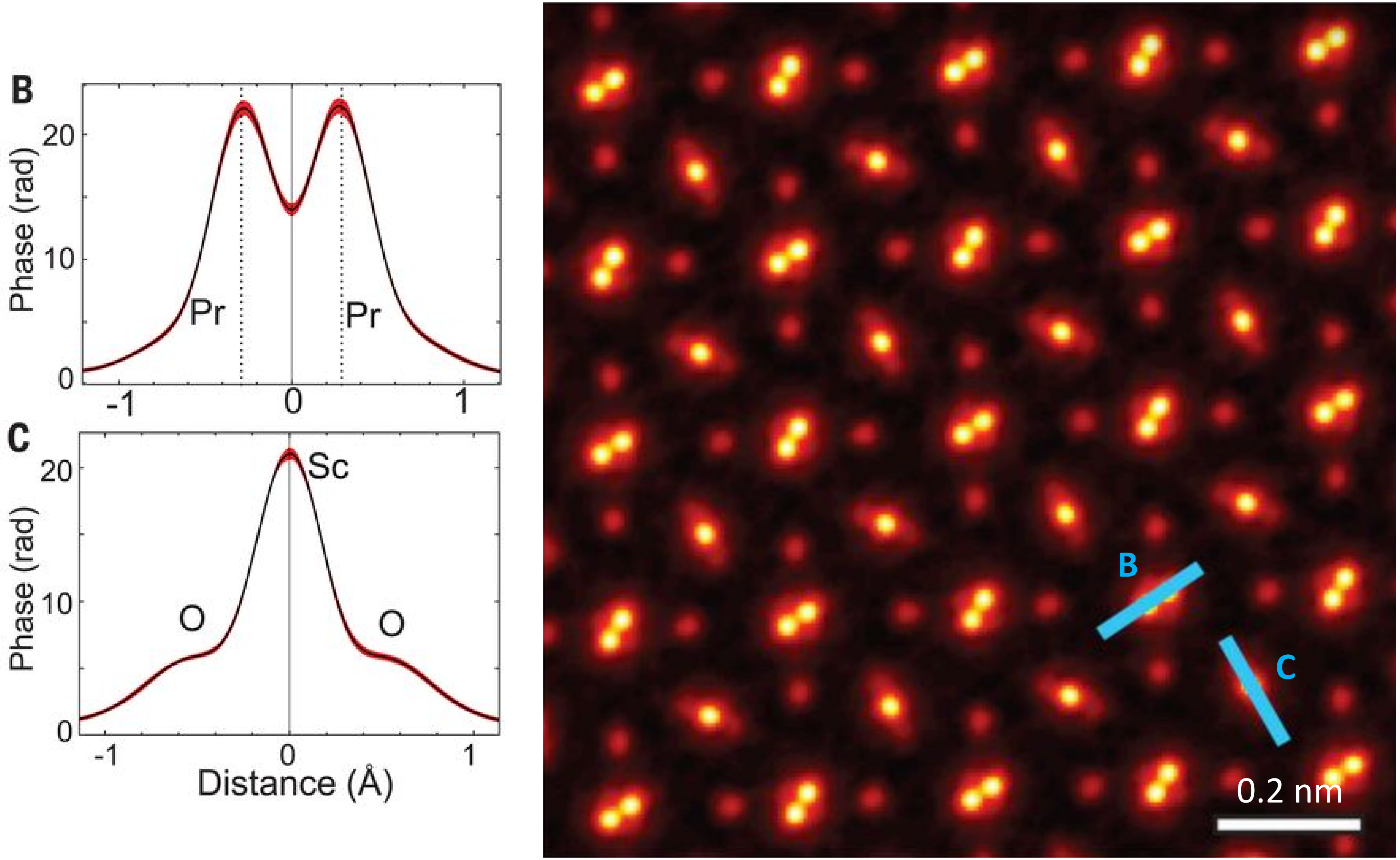
Today in Physics 237: the view through the lens of atomic wavefunctions

- Examples with hydrogen wavefunctions and energies



Ptychographic view of a $PrScO_3$ crystal along the [001] direction, by [Chen et al. 2021](#).

Examples with hydrogen wavefunctions

G&S problem 4.15:

a. Find $\langle r\rangle$ and $\langle r^2\rangle$ for an electron in the ground state of hydrogen. Express your answers in terms of the Bohr radius.

b. Find $\langle x\rangle$ and $\langle x^2\rangle$ for an electron in the ground state of hydrogen. Hint: This requires no new integration – note that $r^2 = x^2 + y^2 + z^2$, and exploit the symmetry of the ground state.

c. Find $\langle x^2\rangle$ in the state $n=2,\ \ell=1,\ m=1$. Hint: this state is not symmetrical in *x, y, z*. Use $x = r\sin\vartheta\cos\varphi$.

a. As we have found, the ground state is $\psi_{100}(r,\vartheta,\varphi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$:

$$\langle r\rangle = \int \psi^* r\psi d\tau = \frac{1}{\pi a^3}\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\vartheta d\vartheta \int_0^{\infty} r^3 e^{-2r/a} dr = \frac{1}{\pi a^3}(2\pi)\left[-\cos\vartheta\right]_0^{\pi}\left(\frac{a^4}{2^4}\int_0^{\infty} u^3 e^{-u} du\right) = \frac{1}{\pi a^3}(4\pi)\left(\frac{a^4}{2^4}3!\right) = \boxed{\frac{3}{2}a} .$$

G&S 4.15 (continued)

For $\langle r^2 \rangle$, the angular integral is 4π again, and the extra factor of r increases the factorial and the number of factors of $a/2$:

$$\langle r^2 \rangle = \frac{1}{\pi a^3}(4\pi)\left(\frac{a^5}{2^5}4!\right) \boxed{= 3a^2} \quad .$$

b. Always use hints. Here it's that the ground state is spherically symmetric, so

$$\langle x \rangle = \langle y \rangle = \langle z \rangle \boxed{= 0,} \; \langle x^2 \rangle = \langle y^2 \rangle = \langle y^2 \rangle = \frac{1}{3}\langle r^2 \rangle \boxed{= a^2} \quad .$$

But if you insist:

$$\langle x \rangle = \int \psi^* r \sin\vartheta \cos\varphi \psi d\tau = \frac{1}{\pi a^3} \overset{0}{\int_0^{2\pi} \cos\varphi d\varphi} \int_0^{\pi} \sin^2\vartheta d\vartheta \int_0^{\infty} r^3 e^{-2r/a} dr \boxed{= 0} \; ,$$

$$\langle x^2 \rangle = \int \psi^* r^2 \sin^2\vartheta \cos^2\varphi \psi d\tau = \frac{1}{\pi a^3} \int_0^{2\pi} \cos^2\varphi d\varphi \int_0^{\pi} \sin^3\vartheta d\vartheta \int_0^{\infty} r^4 e^{-2r/a} dr = \frac{1}{\pi a^3}(\pi)\left(\frac{4}{3}\right)\left(\frac{a^5}{2^5}4!\right) \boxed{= a^2} \quad .$$

G&S 4.15 (continued)

c. As you will find in G&S problem 4.13 on this week's assignment, $\psi_{211}(r,\vartheta,\varphi) = -\frac{1}{\sqrt{\pi a}}\frac{1}{8a^2} r e^{-r/2a}\sin\vartheta e^{i\varphi}$:

$$\left\langle x^2 \right\rangle = \int \psi^* r^2 \sin^2\vartheta \cos^2\varphi \psi d\tau = \frac{1}{\pi a}\left(\frac{1}{64a^4}\right)\int_0^{2\pi}\cos^2\varphi d\varphi \int_0^{\pi}\sin^5\vartheta d\vartheta \int_0^{\infty} r^6 e^{-r/a} dr$$

$$= \frac{1}{\pi a}\left(\frac{1}{64a^4}\right)(\pi)\left(\frac{16}{15}\right)\left(a^7 6!\right) = \boxed{12a^2} \quad .$$

A few useful integrals

p and q are nonnegative integers, and $p!! = p(p-2)(p-4)\ldots(1)$, not to be confused with $(p!)!$.

$$I_E = \int_0^{\pi/2} \sin^{2q} u\,du = \int_0^{\pi/2} \cos^{2q} u\,du = \frac{\pi}{2}\frac{(2q-1)!!}{(2q)!!} = \frac{\pi}{2},\ \frac{\pi}{4}, \frac{3\pi}{16}, \frac{5\pi}{32}, \frac{35\pi}{256}, \ldots$$

$$I_O = \int_0^{\pi/2} \sin^{2q+1} u\,du = \int_0^{\pi/2} \cos^{2q+1} u\,du = \frac{(2q)!!}{(2q+1)!!} = 1, \frac{2}{3}, \frac{8}{15}, \frac{16}{35}, \frac{128}{315}, \ldots$$

$$\int_0^{p\pi/2} \sin^{2q} u\,du = \int_0^{p\pi/2} \cos^{2q} u\,du = pI_E \quad , \quad p = 1, 2, 3, 4$$

$$\int_0^{p\pi/2} \sin^{2q+1} u\,du = I_O\left(1 - \cos\frac{p\pi}{2}\right) \quad , \quad \int_0^{p\pi/2} \cos^{2q+1} u\,du = I_O \sin\frac{p\pi}{2} \quad , \quad p = 1, 2, 3, 4$$

G&S 4.16

G&S problem 4.16 What is the most probable value of *r*, in the ground state of hydrogen? (The answer is not zero!) Hint: First you must figure out the probability that the electron would be found between *r* and *r* + *dr*.

- The probability density, here probability per unit volume, is $p = |\psi_{100}|^2 = \frac{1}{\pi a^3} e^{-2r/a}$. Note, again, that it's spherically symmetric.
- The volume of space for which radius lies between *r* and *r* + *dr* is $d\tau = 4\pi r^2 dr$.
- So the probability *P*(*r*) we're looking for is simply given by $P(r)dr = pd\tau = \frac{4r^2}{a^3} e^{-2r/a} dr$. Differentiate and set to 0:

$$\frac{dP(r)}{dr} = \frac{d}{dr}\left(\frac{4r^2}{a^3} e^{-2r/a}\right) = \frac{8r}{a^3} e^{-2r/a} + \frac{4r^2}{a^3}\left(-\frac{2}{a}\right) e^{-2r/a} = 0 \quad \Rightarrow \quad \boxed{r = a.}$$

G&S 4.20

Believe it or not, this gravity problem has an important point about atomic size. See Lecture 15 for the H formulas.

G&S problem 4.20 Consider the earth–sun system as a gravitational analog to the hydrogen atom.

a. What is the potential energy function (replacing Equation 4.52)? (Let *m* be the mass of Earth, and *M* the mass of the sun.)

b. What is the "Bohr radius," , for this system? Work out the actual number.

c. Write down the gravitational "Bohr formula," and, by equating E_n to the classical energy of a planet in a circular orbit of radius , show that $n=\sqrt{r_o/a_g}$. From this, estimate the quantum number *n* of Earth.

d. Suppose the earth made a transition to the next lower level . How much energy would be released? What would the wavelength of the emitted photon (or, more likely, graviton) be? Express your answer in light years – is the remarkable answer a coincidence?

G&S 4.20 (continued)

a. The potential energy of the Earth-Sun system is $V(r) = -G\frac{Mm}{r}$, compared to $V(r) = -\frac{e^2}{r}$ for hydrogen, in cgs. So e^2 (or $e^2/4\pi\varepsilon_0$ in SI) corresponds to GMm.

b. The Bohr radius is $a = \frac{\hbar^2}{e^2 m_e}$, so $\boxed{a_g = \frac{\hbar^2}{GMm^2}} = 2.34 \times 10^{-136}$ cm .

c. The energy spectrum of H is $E_n = -\frac{m_e e^4}{2\hbar^2}\frac{1}{n^2} \rightarrow \boxed{-\frac{G^2 M^2 m^3}{2\hbar^2}\frac{1}{n^2}}$.

d. And the total energy of a classical orbiting system (force providing centripetal acceleration) is

$$E_c = \frac{1}{2}mv^2 - \frac{GMm}{r_o} = \frac{1}{2}mr_o\left(\frac{v^2}{r_o}\right) - \frac{GMm}{r_o} = \frac{1}{2}mr_o\left(\frac{GM}{r_o}\right) - \frac{GMm}{r_o} = -\frac{GMm}{2r_o} = E_n = -\frac{G^2M^2m^3}{2\hbar^2}\frac{1}{n^2} .$$

So $$n^2 = \frac{GMm^2}{\hbar^2}r_o = \frac{r_o}{a_g} \Rightarrow \boxed{n = \sqrt{r_o/a_g}} \xrightarrow[r_o = 1\text{ AU}]{} 2.5 \times 10^{74}.$$

G&S 4.20 (continued)

- To find n of the lower-energy state is just algebra:

$$\Delta E = E_{n+1} - E_n = -\frac{G^2M^2m^3}{2\hbar^2}\left[\frac{1}{(n+1)^2} - \frac{1}{n^2}\right] = -\frac{G^2M^2m^3}{2\hbar^2 n^2}\left[\frac{1}{\left(1+\frac{1}{n}\right)^2} - 1\right]$$

Take $n \gg 1$ and make a first-order approximation, using the binomial theorem

$$\cong -\frac{G^2M^2m^3}{2\hbar^2 n^2}\left[\left(1-\frac{2}{n}\right)-1\right] = \frac{G^2M^2m^3}{\hbar^2 n^3} = 2.1\times 10^{34}\ \text{erg}$$

$$= \frac{hc}{\lambda} \quad \Rightarrow \quad \lambda = \frac{2\pi\hbar c}{\Delta E} = 2\pi\hbar c\frac{\hbar^2}{G^2M^2m^3}n^3 = c\frac{2\pi\hbar^3}{G^2M^2m^3}\left(\frac{GMm^2r_o}{\hbar^2}\right)^{3/2} = c\times 2\pi\sqrt{\frac{r_o^3}{GM}} = 9.5\times 10^{17}\ \text{cm} \cong 1\ \text{light year}\ .$$

orbital period T

Thus that it comes out to a light year is just to say that its orbital period is a year, so it's no accident. The same ($\lambda = cT$) is true of hydrogen atoms at large n (**Rydberg states**), for which the electrons approach classical behavior.