Workshop: Average values and uncertainties

Quantum aspects of physical chemistry

http://quantum.bu.edu/PLTL/2/2.pdf
Last updated Tuesday, November 15, 2005 12:56:11-05:00

Department of Chemistry, Boston University, Boston MA 02215

The work of Bohr and de Broglie led to the idea that matter must be represented in terms of wavefunctions, and Born introduced the idea that the squared magnitude of a wavefunction at a point determines the probability density that the object described by the wavefunction will be found at that point. This workshop explores how to use these ideas to predict the potential and kinetic energy, and so total energy of a particle from its wavefunction.

Note that it will be helpful to use a programmable calculator, spreadsheet, or other automation tool to carry out the calculations outlined in this workshop.

We will explore lowest energy solutions to the one electron Schrödinger equation

$$\left(-\frac{d^2}{d\rho^2} + v_{\text{eff},Z\ell}(\rho) \right) P_{jZ\ell}(\rho) = \epsilon_{jZ\ell} P_{jZ\ell}(\rho)$$

for the shell amplitude $P_{jZ\ell}$. The potential energy

$$v_{\text{eff},Z\ell}(\rho) = \frac{\ell(\ell+1)}{\rho^2} - \frac{2Z}{\rho}$$

and the total energy $\epsilon = E/(E_h/2) = E/E_r$ are both in rydbergs,

$$E_r = \frac{1}{2}\,\frac{e^2}{4\pi e_0 a_0} = \frac{\hbar^2}{2 m a_0^2} = \frac{m e^4}{32\pi^2 \epsilon_0^2 \hbar^2} = 13.60\,\text{eV} = 2.179\times 10^{-18}\,\text{J},$$

and length $\rho = r/a_0$ is the Bohr radius,

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.5292\,\text{Å}.$$

The fraction of the electron anywhere within $d r$ of the surface of a sphere of radius r is $|P_{jZ\ell}(\rho)|^2\, d\rho$,

$$\int_0^{\pi}\int_0^{2\pi} \left| \psi_{j\ell m}(\rho,\theta,\phi) \right|^2 \rho^2 d\rho \sin\theta\, d\theta\, d\phi = |P_{jZ\ell}(\rho)|^2\, d\rho$$

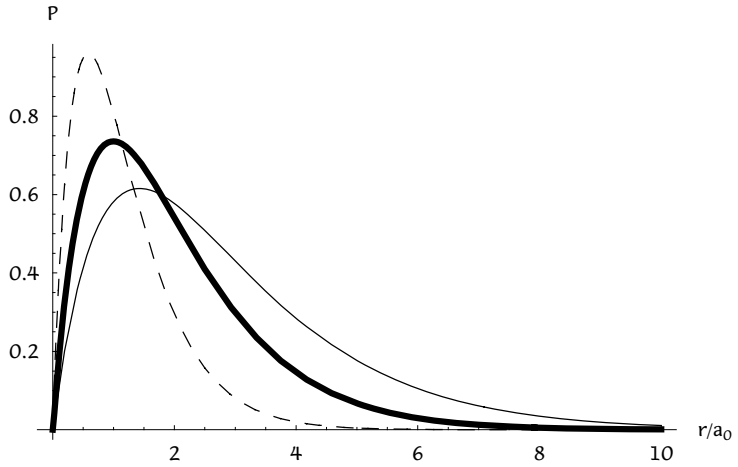
where $\psi_{j\ell m}(\rho,\theta,\phi)$ is the full, three dimensional wavefunction of the electron in the atom. For this reason, $|P_{jZ\ell}(\rho)|^2$ is called the *shell density* of the electron, and this is why we call $P_{jZ\ell}$ the shell amplitude. The fraction of the electron anywhere at all is

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} \left| \psi_{j\ell m}(\rho,\theta,\phi) \right|^2 \rho^2 d\rho \sin\theta\, d\theta\, d\phi = \int_0^{\infty} |P_{jZ\ell}(\rho)|^2\, d\rho = 1$$

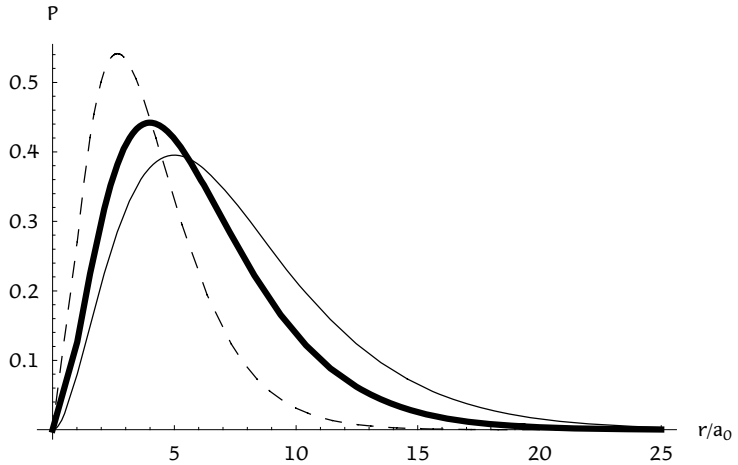
That is, the total probability of finding the electron somewhere is unity.

> 1. What are the units of the shell amplitude?

The figures below show the lowest energy s ($\ell = 0$) and p ($\ell = 1$) shell amplitudes for hydrogen atom ($Z = 1$), together with alternative shell amplitudes that are too diffuse and too compact.



Lowest energy s ($\ell = 0$) shell amplitudes for hydrogen atom. Distance from the nucleus, r, is in units $a_0 = 0.529$ Å. The thick line is the correct shell amplitude and its energy -1; the thin line is a shell amplitude that is too diffuse; and the dashed line is a shell amplitude that is too compact.



Lowest energy p ($\ell = 1$) shell amplitude for hydrogen atom. Distance from the nucleus, r, is in units $a_0 = 0.529$ Å. The thick line is the correct shell amplitude and its energy is -1/4; the thin line is a shell amplitude that is too diffuse; and the dashed line is a shell amplitude that is too compact.

In each case, the correct shell amplitude (thick) results in the correct balance of positive kinetic energy and negative potential energy so that the total energy in a minimum.

> 2. Explain whether you expect the too diffuse s shell amplitude to have more or less kinetic energy relative to the correct s shell amplitude.

> 3. Explain whether you expect the magnitude of the potential energy of the too compact p shell amplitude to be greater or less than that of the correct p shell amplitude.

> 4. Account for the differences between the correct 1s and the 2p shell amplitudes. Hint: Consider $v_{\text{eff},Z\,\ell}(\rho)$.

■ Average distance from nucleus

The way to estimate the average position of the particle, $\langle x \rangle$, is to weight each possible position by the probability that the particle will be found at that position,

$$\langle \rho \rangle = \int_0^\infty | P_{jZ\ell}(\rho) |^2 \ \rho \, d\rho.$$

> 5. Use the table of values below of the 1s shell density to plot the integrand $| P_{1s}(\rho) |^2 \ \rho$. Based on your plot, do you think it is reasonable to limit the averaging to the range $0 \le \rho \le 6$?

ρ	P_{1s}	ρ	P_{1s}
0.0	0.0000	3.2	0.2609
0.2	0.3275	3.4	0.2269
0.4	0.5363	3.6	0.1967
0.6	0.6586	3.8	0.1700
0.8	0.7189	4.0	0.1465
1.0	0.7358	4.2	0.1260
1.2	0.7229	4.4	0.1080
1.4	0.6905	4.6	0.0925
1.6	0.6461	4.8	0.0790
1.8	0.5951	5.0	0.0674
2.0	0.5413	5.2	0.0574
2.2	0.4875	5.4	0.0488
2.4	0.4354	5.6	0.0414
2.6	0.3862	5.8	0.0351
2.8	0.3405	6.0	0.0297
3.0	0.2987	6.2	0.0252

6. Decide on an optimum scheme to evaluate the area under your plot of the integrand.

7. Use your plot of the integrand $|P_{1s}(\rho)|^2\ \rho$ and a 0.4 unit mesh to show that a numerical estimate of the average position is 1.48. What should the units of your answer be? Are the units of your answer correct?

8. The exact answer is $\langle\rho\rangle = 1.5$. How could you improve your calculated value?

9. Does your value for the average position make sense? Could you have anticipated this value, without doing any calculations

10. Why does the exact value differ from the maximum in the shell amplitude?

11. Use the table of values below of the 2p shell density to plot the integrand $|P_{2p}(\rho)|^2\ \rho$. Based on your plot, do you think it is reasonable to limit the averaging to the range $0 \le \rho \le 14$?

ρ	P_{2p}	ρ	P_{2p}
0.0	0.0000	8.0	0.2393
0.5	0.0397	8.5	0.2104
1.0	0.1238	9.0	0.1837
1.5	0.2169	9.5	0.1594
2.0	0.3004	10.0	0.1375
2.5	0.3655	10.5	0.1181
3.0	0.4099	11.0	0.1009
3.5	0.4345	11.5	0.0859
4.0	0.4420	12.0	0.0729
4.5	0.4357	12.5	0.0616
5.0	0.4189	13.0	0.0519
5.5	0.3947	13.5	0.0436
6.0	0.3659	14.0	0.0365
6.5	0.3344	14.5	0.0305
7.0	0.3020	15.0	0.0254
7.5	0.2700	15.5	0.0211

12. Use your plot of the integrand $|P_{2p}(\rho)|^2\ \rho$ and a 1.0 unit mesh to show that a numerical estimate of the average position is 4.97.

13. The exact value is $\langle\rho\rangle = 5.0$. Why is the 2p average distance so much greater than the 1s average distance?

■ Average potential energy

The average potential energy corresponding to a one electron shell amplitude $P_{jZ\ell}(\rho)$ is $\langle \text{PE} \rangle = \int_0^\infty |P_{jZ\ell}(\rho)|^2\ v_{\text{eff},Z\ell}(\rho)\, d\rho$.

14. Show that the average potential energy corresponding to the hydrogen atom 1s shell amplitude is $\langle \text{PE} \rangle = -\int_0^\infty |P_{1s}(\rho)|^2\ 2/\rho\, d\rho$.

15. Use the table of values given above of the 1s shell density to plot the integrand $-|P_{1s}(\rho)|^2\ 2/\rho$. Based on your plot, do you think it is reasonable to limit the averaging to the range $0 \le \rho \le 4$?

16. Why is the integration range less in this case than for the calculation of $\langle\rho\rangle$?

17. Use your plot of the integrand $-\,|\,P_{1s}(\rho)\,|^2\;2/\rho$ and a 0.2 unit mesh to show that a numerical estimate of the average potential energy is -1.87. What should the units of your answer be? Are the units of your answer correct?

18. The exact answer is $\langle -2/\rho \rangle = -2.0$. How could you improve your calculated value?

19. Show that the average potential energy corresponding to the hydrogen atom 2p shell amplitude is $\langle \mathrm{PE} \rangle = \int_0^\infty \left|\, P_{jZ\ell}(\rho) \,\right|^2 \left(\frac{2}{\rho^2} - \frac{2}{\rho} \right) d\rho$.

20. Use the table of values given above of the 2p shell density to plot the integrand $|\,P_{2p}(\rho)\,|^2\;(2/\rho^2 - 2/\rho)$. Based on your plot, do you think it is reasonable to limit the averaging to the range $0 \le \rho \le 10$?

21. Use your plot of the integrand $|\,P_{2p}(\rho)\,|^2\;(2/\rho^2 - 2/\rho)$ and a 1.0 unit mesh to show that a numerical estimate of the average potential energy is -0.334. What should the units of your answer be? Are the units of your answer correct?

22. The exact value of the 2p potential energy is $-1/3$. Why, with such a coarse integration mesh, is the approximate answer so close to the exact value?

23. Why is the 2p potential energy so much less than the 1s potential energy?

■ Average kinetic energy

The kinetic energy corresponding to one electron atom shell amplitude is the expectation (average) value

$$\langle \mathrm{KE} \rangle = -\int_0^\infty P_{jZ\ell}(\rho)\,\frac{d^2\,P_{jZ\ell}(\rho)}{d\rho^2}\,d\rho.$$

To estimate the value of the average for a numerical wavefunction, we can approximate the second derivative in the integrand as

$$\left(\frac{d^2\psi}{d\rho^2}\right)_{\rho_j} = \left(\frac{\psi(\rho_{j+1}) - \psi(\rho_j)}{s} - \frac{\psi(\rho_j) - \psi(\rho_{j-1})}{s}\right)\Big/ s = \frac{\psi(\rho_{j+1}) - 2\,\psi(\rho_j) + \psi(\rho_{j-1})}{s^2}$$

Since the second derivative is proportional to ρ^2, it is appreciable only over a smaller range than the shell amplitude.

24. Use the table of values given above of the 1s shell density to the integrand $-P_{1s}(\rho)\,d^2\,P_{1s}(\rho)/d\rho^2$ for the hydrogen atom 1s shell amplitude. Based on your plot, do you think it is reasonable to limit the averaging to the range $0 \le \rho \le 5$?

25. Use your plot of the integrand $-P_{1s}(\rho)\,d^2\,P_{1s}(\rho)/d\rho^2$ and a 0.5 unit mesh to show that a numerical estimate of the kinetic energy is 0.89. What should the units of your answer be? Are the units of your answer correct?

26. The exact answer for the average kinetic energy is 1.0. How could you improve your calculated value?

27. In a similar way, using a 0.5 unit mesh over the range $0 \le \rho \le 14$, you could estimate the 2p average kinetic energy to be 0.086, very close to the exact value 0.083. Why is the 2p kinetic energy so much less than the 1s kinetic energy?

■ Average total energy

The average total energy is $\langle E \rangle = \langle \mathrm{PE} \rangle + \langle \mathrm{KE} \rangle$.

$$\langle E \rangle = \langle \mathrm{PE} \rangle + \langle \mathrm{KE} \rangle$$

28. The lowest energy s shell amplitude has energy -1. How does this compare with the values computed here?

29. Both the more diffuse and the more compact 1s shell amplitudes have higher energy than the correct shell amplitude. Explain, for each case, whether kinetic energy is too positive or potential energy is not negative enough.

30. The lowest energy p shell amplitude has energy $-1/4$. How does this compare with the values computed here?

31. Both the more diffuse and the more compact 2p shell amplitudes have higher energy than the correct shell amplitude. Explain, for each case, whether kinetic energy is too positive or potential energy is not negative enough.