

### 1. Interacting particles

In the previous assignment you studied a system of two particles, specifically a pair of noninteracting harmonic oscillators. Denoting the particles' positions as  $x$  and  $y$ , the Hamiltonian for that model can be written

$$\mathcal{H}_{\text{noninteracting}} = h(x) + h(y), \quad \text{where}$$

$$h(x) = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2} x^2 \quad \text{and} \quad h(y) = -\frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} y^2$$

That problem can be solved exactly, because the particles do not interact with each other.

Here we will add an interaction to the two-particle system, a potential energy contribution  $ax^4y^4$  that depends on *both* particles' positions. The strength of this interaction is set by the constant parameter  $a$ . We will take  $a > 0$ , so that the two particles are discouraged from simultaneously wandering far from the origin ( $x = 0, y = 0$ ). The resulting Hamiltonian,

$$\mathcal{H} = h(x) + h(y) + ax^4y^4, \quad (1)$$

looks only a little more complicated than  $\mathcal{H}_{\text{noninteracting}}$ , but the problem can no longer be solved exactly.

(i) Make a surface plot and/or contour plot of  $x^4y^4$  as a function of  $x$  and  $y$ . What features of your plot indicate that our interacting oscillators are discouraged from simultaneously wandering far from the origin?

(ii) To apply our computational approach to the interacting oscillators, we just need to add in the matrix element  $\langle \phi_A | x^4y^4 | \phi_B \rangle$ . That quantity can be determined by differentiating the generating function from Problem Set 2, but we'll spare you the hard work by providing the integral

$$\begin{aligned} g(x_A, x_B) &= \int_{-\infty}^{\infty} dx e^{-\alpha(x-x_A)^2} x^4 e^{-\alpha(x-x_B)^2} \\ &= s(x_A, x_B) \left[ \frac{3}{16\alpha^2} + \frac{3}{8\alpha}(x_A + x_B)^2 + \frac{1}{16}(x_A + x_B)^4 \right], \end{aligned}$$

where

$$s(x_A, x_B) = \int dx e^{-\alpha(x-x_A)^2} e^{-\alpha(x-x_B)^2} = \sqrt{\frac{\pi}{2\alpha}} \exp \left[ -\frac{\alpha}{2}(x_A - x_B)^2 \right]$$

is the familiar overlap of 1-d Gaussian functions centered at  $x_A$  and  $x_B$ .

Using these results, write  $\langle \phi_A | x^4y^4 | \phi_B \rangle$  in terms of  $\alpha$ ,  $x_A$ ,  $y_A$ ,  $x_B$ , and  $y_B$ . (As a check, you should find for the case  $\alpha = 1/2$  and  $x_A = y_A = x_B = y_B = 0$  that  $\langle \phi_A | x^4y^4 | \phi_B \rangle = 9\pi/16$ ).

(iii) Build a Python program to solve Schrödinger's equation for the interacting oscillators. Start with the noninteracting 2-d code of Problem Set 3 (either your own or our's).

As a first step, compute the matrix elements of  $x^4y^4$  and store them as a  $K \times K$  matrix  $G$  with elements

$$G_{AB} = \langle \phi_A | x^4y^4 | \phi_B \rangle$$

(iv) From the noninteracting oscillator code, you should already have computed and stored values of  $\langle \phi_A | \phi_B \rangle$  as a matrix  $S$ , and values of  $\langle \phi_A | h(x) + h(y) | \phi_B \rangle$  as a matrix  $H$ . Construct the full Hamiltonian matrix by adding in the interaction,  $H = H + a * G$ .

(v) Now find the eigenvalues of  $\mathbf{S}^{-1} \cdot \mathcal{H}$  to determine an estimate  $\tilde{E}_0$  for the ground state energy. Using  $K = (2n + 1)^2 = 225$  Gaussian basis functions (with width parameter  $\alpha = 2$ , and spaced by  $\Delta x = 0.5$  in  $x$  and  $y$  directions), compute  $\tilde{E}_0$  for a weak interaction  $a = 0.005$ . You should find that  $\tilde{E}_0 \approx 1.002614$ .

(vi) Repeat your calculation of  $\tilde{E}_0$  for interaction strengths  $a = 0.001, 0.01, 0.05, 0.1, 0.5, 1$ , and  $10$ . Report your results in a table.

(vii) Although the interacting oscillator problem cannot be solved exactly, a good approximation can be made when the interaction is weak. In a class like Chem 120 A, you should learn how to make such an estimate using perturbation theory (PT). Here, we will just quote the result,

$$\begin{aligned} E_0^{(\text{PT})} &= E_0(0) + a \langle \psi_0 | x^4 y^4 | \psi_0 \rangle \\ &= 1 + 9a/16 \end{aligned}$$

where  $|\psi_0\rangle$  is the noninteracting ground state. Evaluate  $E_0^{(\text{PT})}$  for the same  $a$  values as in part (vi), and add them to your table as a new column. In a third column, show the relative error of perturbation theory,

$$\text{error} = \frac{E_0^{(\text{PT})} - \tilde{E}_0}{\tilde{E}_0}$$

Over what range of  $a$  is the perturbation theory estimate accurate to within 1%?

(viii) For the case  $a = 1$ , make a contour plot of the ground state wavefunction over a range of  $x$  and  $y$  values spanning  $-2.5$  to  $2.5$ . How does it differ from the noninteracting case ( $a = 0$ )? Can you rationalize this difference?

(ix) Make similar contour plots for a few other interaction strengths:  $a = 0.001$ ,  $a = 0.01$ ,  $a = 0.1$ ,  $a = 10$ , and  $a = 100$ . To your eye, how large must  $a$  be to significantly modify the structure of the ground state? How does this observation compare with the range of validity of perturbation theory you found in part (vii)?

## 2. *d* orbitals (see Lecture 8 notebook as well!)

In class we wrote a program `H_atom_ptype` to estimate the  $2p_z$  state of a hydrogen atom.

(i) Add a thorough set of comments to this program, which is available on bcourses.

(ii) The  $n = 3$  shell of the hydrogen atom includes 5 *d* orbitals, one of which is sketched below.

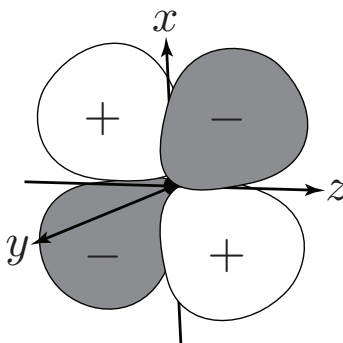


Figure 1: Wavefunction of the  $d_{xz}$  orbital of a hydrogen atom. The sign of the wavefunction is indicated in four different regions. The four lobes depict surfaces on which the wavefunction has a constant value.

Lacking radial symmetry, this wavefunction clearly cannot be represented as a sum of Gaussian functions that are all centered at the origin.

How could you arrange Gaussian functions to obtain a linear combination with  $d$ -type symmetry? Specifically, how many would you need, where would you center them, and how would they be added/subtracted? You can give your answer in a few precise sentences. Alternatively, you can make a plot (by hand or with a computer) in the  $xz$ -plane indicating the placement and contraction coefficient of each Gaussian.

(iii) In the program `H_atom_ptype`, we created  $p$ -type basis functions as contractions of pairs of Gaussians. Using three such basis functions (with width parameters  $\alpha = 0.6, 0.1$  and  $0.02$ ), we obtained a good estimate of the  $2p_z$  orbital and its energy.

Modify the program to make  $d_{xz}$ -type basis functions as contractions of Gaussians. Use three such basis functions, with width parameters  $\alpha = 0.42, 0.045$  and  $0.014$ .

Note that the value of `L` will be different than in our  $p$  orbital code.  $L \times K$  matrices like `widths` and `contraction_coeffs` will therefore have different dimensions, and you will need to fill in their values. You might find it helpful to write out values of  $\alpha_{A\mu}$ ,  $d_{A\mu}$ , etc. on a piece of paper before constructing these matrices in Python.

(iv) Run your code to find the eigenvalues and eigenvectors of  $\mathbf{S}^{-1} \cdot \mathcal{H}$ , which should provide an estimate of hydrogen's  $3d_{xz}$  orbital.

(v) How does the energy you obtained compare with the exact  $n = 3$  energy level?

(vi) Make a contour plot of your wavefunction in the  $xz$ -plane.