10302 Electronic Structure

Problem Set 5
Pseudopotential for a spherical well.

Spring 2021

In this problem set you will construct a pseudopotential for a simple spherical well potential. The solution to the problem set including the required numerical work can be found in the IPython notebook "pseudopotential.ipynb" at campusnet.

The spherical well potential: Consider a potential with a constant value $V_0 < 0$ inside a cutoff radius r_c. Outside the cutoff radius the potential is zero. Write down the radial equation corresponding to this potential in atomic units (use the function $\chi(r) = rR(r)$, where $R(r)$ is the radial part of the wavefunction; see for example Equation (7.23) in Kohanoff). In the following we shall consider only the s-channel ($l = 0$). Show that by rescaling $V_0 r_c^2 \to V_0$ and $\varepsilon r_c^2 \to \varepsilon$ (ε is the eigenvalue) we can without any loss of generality consider only $r_c = 1$.

The eigenstates: In the following we consider a spherical well with radius $r_c = 1$ and depth $V_0 = -60$. Write down the solutions to the radial equation inside and outside the sphere and find the eigenvalues by matching the logarithmic derivative at the boundary (use IPython yourself or the solution notebook). There should be three solutions corresponding to bound states.

The pseudowave function: We now want to construct a pseudopotential for energies around the $3s$-state by defining a $3s$ pseudowave function. Define a sinusoidal pseudofunction $\tilde{\chi}$ that has the same logarithmic derivative at the sphere boundary as the real $3s$-state.

The pseudopotential: Construct the pseudopotential $\tilde{v}(r)$ so that the pseudowave function becomes an eigenstate of the potential at the right energy, i.e.

$$-\frac{1}{2}\tilde{\chi}''(r) + \tilde{v}(r)\tilde{\chi}(r) = \varepsilon_{3s}\tilde{\chi}(r).$$

Logarithmic derivatives: Plot the logarithmic derivatives (at $r = r_c$) for the real potential and the pseudopotential as a function of energy.

Normconservation: Construct a new pseudowave function so that it gets the same norm inside the sphere as the real wave function. Note that two free parameters are required to make the function match at the boundary *and* normalize it. You can for example choose $\tilde{\chi}(r) = r + ar^3 + br^5$, then use IPython to determine a and b. Plot the pseudopotential.

Logarithmic derivatives revisited: Again plot the logarithmic derivatives as a function of energy. The differential equation can be solved by numerical integration. Does the norm conservation improve the energy dependence?