

## Abstract

A single document copy of these notes, as well as a mirror of every note, can be found at [connorduncan.xyz/notes](http://connorduncan.xyz/notes) We continue with degenerate perturbation theory, taking

$$\langle \varphi_{n,j} | \left( \hat{H}_0 | \varphi_n^{(1)} \rangle + \hat{H}_1 \sum_{i=1}^N c_i | \varphi_{n,i}^{(0)} \rangle \right) = E_n^{(0)} | \varphi_n^{(1)} \rangle + E_n^{(1)} \sum_{i=1}^N c_i | \varphi_{n,i}^{(0)} \rangle$$

which starts simplifying out to

$$\sum_{i=1}^N \langle \varphi_{n,j} | \hat{H}_1 | \varphi_{n,i}^{(0)} \rangle c_i = E_n^{(1)} c_i$$

$$\sum_{i=1}^N [\hat{H}_1]_{ji} c_i = E_n^{(1)} c_i$$

where the final equality is just matrix multiplication of a vector.

### 0.0.1 Hydrogen Atom

Take

$$H_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{|\hat{r}|}$$

$$H_1 = -\mu_e \cdot \vec{E} = -e\hat{r} \cdot \vec{E} = eE\hat{z}$$

$$H = H_0 + H_1$$

We're allowed to ignore spin here, since the electric field points along the spin axis.

**Review: Spectrum of Hydrogen Atom** Given by quantum numbers,

$$| \varphi_{n,\ell,m}^{(0)} \rangle = | n, \ell, m \rangle$$

where  $n$  is the principal quantum number,  $\ell$  is related to  $L^2$ , and  $m$  is related to  $L^z$ . For higher values of  $n$ , we have an increasing number of allowable values for  $\ell$ , e.g. for  $n = 1$  only  $\ell = 0$  is allowed, but for  $n = 3$ ,  $\ell \in \{0, 1, 2\}$ .<sup>1</sup>

**Nondegenerate  $n = 1$**  Now, we want to ask ourselves what

$$E_{1,0,0}^{(1)} = \mathcal{E} \langle 1, 0, 0 | \hat{z} | 1, 0, 0 \rangle = 0$$

Since we know it's invariant under rotation, we have the last equality. This means we need to go to second order in our energy correction, so we want

$$E_{1,0,0}^{(2)} = \mathcal{E}^2 \sum_{n=1}^{\infty} \sum_{\ell,m} \frac{|\langle n, \ell, m | \hat{z} | 1, 0, 0 \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

This sum is really hard to evaluate, but we do know that it converges, and it's a challenge problem to show that it does. We note that the state cannot ever mix different values of  $m$ , from symmetry arguments.

**Degenerate  $n = 2$**  This is cool for the nondegenerate case where  $n = 1$ , but what about the case where  $n = 2$ ? It might be degenerate! This is something different. Our basis can be written as

$$|2, 0, 0\rangle \quad |2, 1, 0\rangle \quad |2, 1, 1\rangle \quad |2, 1, -1\rangle$$

If we didn't know any better, it is actually possible to write this matrix out in its full glory. Altman did it on the board, but was pretty clear that it's "boring to do", and unnecessary. The question he poses is whether or not there's a simplification that can make this problem fun. For one thing, many matrix elements are actually 0 by symmetry arguments, so we can just eliminate those as contenders immediately. The way he keeps posing this argument is as a statement about integrating over functions that are odd under parity. The final form of the matrix he writes down is roughly

$$\hat{H} = -\mathcal{H} \begin{bmatrix} 0 & \langle 2, 0, 0 | \hat{z} | 2, 1, 0 \rangle & 0 & 0 \\ \langle 2, 1, 0 | \hat{z} | 2, 0, 0 \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}$$

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<sup>1</sup>TODO: review this in townsend.