Kramers' Relation

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1 Introduction

Kramers' relation, named after the Dutch physicist Hans Kramers, is a relationship between expectation values of "nearby" powers of r for the hydrogen atom:

$$\frac{s+1}{n^2}\langle r^s\rangle - (2s+1)a\langle r^{s-1}\rangle + \frac{s}{4}[(2l+1)^2 - s^2]a^2\langle r^{s-2}\rangle = 0$$

The relation is very important when computing, specifically, perturbative corrections to the hydrogen spectrum, as those computations require expectation values of the radial Hamiltonian (which has powers of r such as r^{-1} and r^{-2}) and potentially perturbative corrections that have higher (negative) powers of r. Having this relation handy makes a lot of those calculations go more quickly.

This derivation is going to require the solution to the hydrogen atom to be known: the Hamiltonian, the wavefunctions, the energy spectrum, etc. To solve Kramers' relation for all $s > -1$ is straightforward, and will be shown, but to solve for any $s \leq -1$ requires one of these s values to already be known, for instance $\langle r^{-2}\rangle$. The Feynman-Hellmann theorem allows for an easy computation of this, which I derive in the appendix, as well as apply to compute $\langle r^{-2}\rangle$ explicitly, allowing for $\langle r^s\rangle$ to be computed for all values of s using Kramers' relation.

2 The Derivation of the Relation

The radial wave equation for the hydrogen atom is typically written as:

$$H_r R_{nl}(r) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - ke^2\frac{1}{r^2}\right] R_{nl}(r) = E_n R_{nl}(r) \tag{1}$$

where the energy is:

$$E_n = -\frac{\hbar^2}{2m}\frac{1}{n^2a^2} \tag{2}$$

where a is the Bohr radius, defined as $\hbar^2/kme^2$. A more useful form of the above equation, however, is to make the typical substitution $u(r) = rR(r)$, and then express the radial wave equation as:

$$u'' = \left[\frac{l(l+1)}{r^2} - \frac{2}{ar} + \frac{1}{n^2a^2}\right] u \tag{3}$$

Note that I've dropped the labels of nl; these are implied by their presence in the above equation.

Notice the terms we have in the above equation: r^{-2}, r^{-1}, and r^0. If we multiply both sides by r^s, then we'll get exactly the powers of r that we need for Kramer's relation:

$$r^s u'' = \left[l(l+1)r^{s-2} - \frac{2}{a}r^{s-1} + \frac{1}{n^2a^2}r^s\right] u$$

Now what we need to do is multiply both sides by $u^* = u$ and integrate. Then, we'll have:

$$\int u r^s u'' dr = l(l+1)\left\langle r^{s-2}\right\rangle - \frac{2}{a}\left\langle r^{s-1}\right\rangle + \frac{1}{n^2a^2}\left\langle r^s\right\rangle \tag{4}$$

What we need to do is to figure out how to deal with the integral on the left-hand-side. Luckily, this integral is set up so that it includes a factor of ur^s and a factor of $u''dr$. If we integrate by parts, it will take two steps to convert the u'' to a u, resulting in an integral like $\int uf(r)udr$ – i.e. an expectation value – and during those two steps, the power of r will drop by one or two, so we'll have powers like r^s, r^{s-1}, and r^{s-2}, exactly as we'd like! Integration by parts makes perfect sense to use, then, to reduce the integral on the left-hand-side of the above equation into additional factors of expectation values of these powers of r.

First, note that the integral goes from $r = 0$ to $r = \infty$, and u equals zero at both limits (because R decreases exponentially as $r \to \infty$, beating the factor of r that increases linearly), so the terms in the integration by parts that are evaluated at these limits will always result in zero, since they will have some dependence on u. Note that I'll be using the notation:

$$\int w dv = -\int v dw$$

for the integration by parts; this way, my choice in how to perform the integration will be clear. For the first step of the integration process, I'll choose $w = ur^s$ and $dv = u''dr$, so integration by parts yields:

$$\int u r^s u'' dr = -\underbrace{\int u' r^s u' dr}_{I_1} - s\underbrace{\int u r^{s-1} u' dr}_{I_2} \tag{5}$$

where I have called the first integral on the right-hand-side I_1 and the second integral I_2 for brevity. Each of these integrals will also need to be evaluated.

For I_1, I'll make the seemingly-odd choice of $w = (u')^2$ and $dv = r^s dr$; if I had chosen something similar to before, like $w = u'r^s$ and $dv = u'dr$, I'd get a recursion relationship that wouldn't be helpful. So, the integration by parts results in:

$$I_1 = \int u' r^s u' dr = -\frac{2}{s+1}\int u' r^{s+1} u'' dr \tag{6}$$

I already have an equation for u'' in terms of u (the radial wave equation), so ultimately I'm going to be solving integrals like $u'r^k u$, so let's figure out what those integrals yield before plugging u'' into the above equation. Choosing $w = ur^k$ and $dv = u'dr$, integration by parts yields:

$$\int u' r^k u dr = -\int u' r^k u dr - k\int u r^{k-1} u dr$$

Pulling the first integral to the left-hand-side and noting the second integral is just the expectation value of r^{k-1}, we find:

$$\int u' r^k u dr = -\frac{k}{2}\left\langle r^{k-1}\right\rangle$$

Now we want to plug our radial wave equation into I_1, equation (6), and use the above result to evaluate it:

$$\int u' r^{s+1} u'' dr = \int u' r^{s+1} \left[\frac{l(l+1)}{r^2} - \frac{2}{ar} + \frac{1}{n^2 a^2}\right] u dr$$
$$= l(l+1) \int u' r^{s-1} u dr - \frac{2}{a} \int u' r^s u dr + \frac{1}{n^2 a^2} \int u' r^{s+1} u dr$$
$$= -\frac{l(l+1)(s-1)}{2} \langle r^{s-2} \rangle + \frac{s}{a} \langle r^{s-1} \rangle - \frac{s+1}{2n^2 a^2} \langle r^s \rangle$$

Thus, the integral I_1 equals:

$$I_1 = \frac{l(l+1)(s-1)}{(s+1)} \langle r^{s-2} \rangle - \frac{2s}{a(s+1)} \langle r^{s-1} \rangle + \frac{1}{n^2 a^2} \langle r^s \rangle$$

We can evaluate the integral I_2 with the formula above:

$$I_2 = s \int u r^{s-1} u' dr = -\frac{s(s-1)}{2} \langle r^{s-2} \rangle$$

So, our original integral, given by equation (5), is:

$$\int u r^s u'' dr = -I_1 - I_2 = -\frac{l(l+1)(s-1)}{(s+1)} \langle r^{s-2} \rangle + \frac{2s}{a(s+1)} \langle r^{s-1} \rangle - \frac{1}{n^2 a^2} \langle r^s \rangle + \frac{s(s-1)}{2} \langle r^{s-2} \rangle$$

Now, going all the way back to the start, we see the above result is only the left-hand-side of equation (4), so we can set it equal to the left-hand-side and solve:

$$-\frac{l(l+1)(s-1)}{(s+1)} \langle r^{s-2} \rangle + \frac{2s}{a(s+1)} \langle r^{s-1} \rangle - \frac{1}{n^2 a^2} \langle r^s \rangle + ...$$
$$... + \frac{s(s-1)}{2} \langle r^{s-2} \rangle = l(l+1) \langle r^{s-2} \rangle - \frac{2}{a} \langle r^{s-1} \rangle + \frac{1}{n^2 a^2} \langle r^s \rangle$$

If we multiply both sides by $2(s+1)$ and group everything to the left-hand-side, we arrive at:

$$-2l(l+1)(s-1) \langle r^{s-2} \rangle + \frac{4s}{a} \langle r^{s-1} \rangle - \frac{2(s+1)}{n^2 a^2} \langle r^s \rangle + s(s-1)(s+1) \langle r^{s-2} \rangle - ...$$
$$... - 2l(l+1)(s+1) \langle r^{s-2} \rangle + \frac{4(s+1)}{a} \langle r^{s-1} \rangle - \frac{2(s+1)}{n^2 a^2} \langle r^s \rangle = 0$$

Notice that combining the $\langle r^{s-2} \rangle$ terms gives a coefficient of:

$$-2l(l+1)(s-1) - 2l(l+1)(s-1) + s(s-1)(s+1) = -4l(l+1)s + s(s^2-1)$$
$$= -s(4l^2 + 4l - s^2 + 1) = -s\left[(2l+1)^2 - s^2\right]$$

The coefficient of the $\langle r^{s-1} \rangle$ term becomes $4(2s+1)/a$, and the coefficient of the $\langle r^s \rangle$ term becomes $-4(s+1)/n^2 a^2$. Putting this all together, our above equation becomes:

$$-s\left[(2l+1)^2 - s^2\right] \langle r^{s-2} \rangle + \frac{4(2s+1)}{a} \langle r^{s-1} \rangle - \frac{4(s+1)}{n^2 a^2} \langle r^s \rangle = 0$$

Finally, multiplying the above equation by $-a^2/4$, and re-ordering from r^s to r^{s-2}, we have Kramers' relation:

$$\frac{s+1}{n^2} \langle r^s \rangle - (2s+1) a \langle r^{s-1} \rangle + \frac{s}{4}\left[(2l+1)^2 - s^2\right] a^2 \langle r^{s-2} \rangle = 0 \tag{7}$$

3 Solutions of the Relation

The main application of Kramers' relation is that of computing perturbative corrections to the hydrogen atom, such as for the fine structure or hyperfine structure of hydrogen. In order to see this in action, let's compute some particular solutions to Kramers' relation.

First, the $\boldsymbol{s = 0}$ solution yields:

$$\frac{1}{n^2} \langle r^0 \rangle - a \langle r^{-1} \rangle = 0$$

So, re-arranging, we find the expectation value of $1/r$:

$$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2 a} \tag{8}$$

Notice also the $\boldsymbol{s = 1}$ solution yields:

$$\frac{2}{n^2} \langle r^1 \rangle - 3a \langle r^0 \rangle + \frac{1}{4} \left[(2l+1)^2 - 1 \right] a^2 \langle r^{-1} \rangle = 0$$

Since we just found $\langle r^{-1} \rangle$, we can solve the above for $\langle r \rangle$. We'll see that setting $\boldsymbol{s = 2}$ will allow us to solve for $\langle r^2 \rangle$, and so on.

However, we run into a problem when trying to go to larger negative powers of r^s, such as trying to find $\langle r^{-2} \rangle$ (by setting $s = -1$, for instance): the best we'll be able to do is to find an equation for $\langle r^{-2} \rangle$ in terms of $\langle r^{-3} \rangle$. Going to progressively larger (negative) powers keeps the problem going – unless we can solve for one along the chain, e.g. $\langle r^{-2} \rangle$ or $\langle r^{-3} \rangle$, then Kramers' relation will never allow us to solve for any value of s below -1. This is seen by checking the $\boldsymbol{s = -1}$ case:

$$a \langle r^{-2} \rangle - \frac{1}{4} \left[(2l+1)^2 - 1 \right] a^2 \langle r^{-3} \rangle = 0$$

As we can see, without knowing either $\langle r^{-2} \rangle$ or $\langle r^{-3} \rangle$, we can't solve for the other. A common way to circumvent this problem is to use the Feynman-Hellmann theorem to compute $\langle r^{-2} \rangle$, which allows for all subsequent solutions for $s < -2$ to be found using Kramers' relation. The Feynman-Hellmann theorem, and the computation of $\langle r^{-2} \rangle$ itself using the theorem, are presented in the appendix; I'll merely present the result here:

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + \frac{1}{2}) n^3 a^2} \tag{9}$$

Knowing $\langle r^{-2} \rangle$, we can solve the above $s = -1$ solution to Kramers' relation for $\langle r^{-3} \rangle$:

$$\langle r^{-3} \rangle = \frac{4}{a[(2l+1)^2 - 1]} \langle r^{-2} \rangle = \frac{4}{[(2l+1)^2 - l](l + \frac{1}{2}) n^3 a^3}$$

Notice that $(2l+1)^2 - 1 = 4l^2 + 4l + 1 - 1 = 4l(l+1)$, so the above equation results in:

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{l(l + \frac{1}{2})(l+1) n^3 a^3} \tag{10}$$

Now that the negative s solutions have been started, one could compute $\langle r^s \rangle$ for all values of s using Kramers' relation.

A Feynman-Hellmann Theorem

Imagine we had a Hamiltonian H with normalized eigenstates $|\psi\rangle$ such that:

$$H|\psi\rangle = E|\psi\rangle$$

If we considered some parameter λ that we could express the Hamiltonian, the states, and the energies in terms of, then the above equation would become:

$$H(\lambda)|\psi(\lambda)\rangle = E(\lambda)|\psi(\lambda)\rangle \tag{11}$$

This, for normalized states, means that:

$$E(\lambda) = \langle\psi(\lambda)| H(\lambda) |\psi(\lambda)\rangle$$

Now we want to consider taking the derivative of the energy with respect to this parameter λ. Applying the product rule to the right-hand-side, we see that:

$$\frac{dE(\lambda)}{d\lambda} = \left(\frac{d}{d\lambda}\langle\psi(\lambda)|\right) H(\lambda)|\psi(\lambda)\rangle + \left\langle\psi(\lambda)\left|\frac{dH(\lambda)}{d\lambda}\right|\psi(\lambda)\right\rangle + \langle\psi(\lambda)| H(\lambda)\left(\frac{d}{d\lambda}|\psi(\lambda)\rangle\right)$$

For the first and final terms on the right-hand-side of the above equation, we can apply $H(\lambda)$ right-ward and left-ward, respectively, yielding:

$$\frac{dE(\lambda)}{d\lambda} = E(\lambda)\left(\frac{d}{d\lambda}\langle\psi(\lambda)|\right)|\psi(\lambda)\rangle + \left\langle\psi(\lambda)\left|\frac{dH(\lambda)}{d\lambda}\right|\psi(\lambda)\right\rangle + E(\lambda)\langle\psi(\lambda)|\left(\frac{d}{d\lambda}|\psi(\lambda)\rangle\right)$$

Notice, then, that the first and third terms above are simply an example of the product rule:

$$\left(\frac{d}{d\lambda}\langle\psi(\lambda)|\right)|\psi(\lambda)\rangle + \langle\psi(\lambda)|\left(\frac{d}{d\lambda}|\psi(\lambda)\rangle\right) = \frac{d}{d\lambda}\langle\psi(\lambda)|\psi(\lambda)\rangle$$

Here's the final step of the derivation: recall that we required that the states be normalized. Thus, for any parameter λ, $\langle\psi(\lambda)|\psi(\lambda)\rangle = 1$, and so the above term equals zero. Therefore, our above equation for $dE/d\lambda$ simply results in:

$$\frac{dE(\lambda)}{d\lambda} = \left\langle\psi(\lambda)\left|\frac{dH(\lambda)}{d\lambda}\right|\psi(\lambda)\right\rangle \tag{12}$$

This equation is known as the Feynmann-Hellmann theorem[1].

Using the Feynman-Hellmann theorem, I can derive many interesting results. Most important to this note is the derivation of $\langle r^{-2}\rangle$ for the hydrogen atom. To do so, we'll express our (radial) Hamiltonian in the usual way:

$$H = -\frac{\hbar^2}{2m}\frac{d^2}{dr^2} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - \frac{e^2}{4\pi\epsilon_0 r}$$

and we'll express the energy of a state $|\psi_{nlm}\rangle$ in terms of $n = j_{\max} + l + 1$. This is because, in order to compute $\langle r^{-2}\rangle$, we need to choose $\lambda = l$ in the Feynman-Hellmann theorem, so E needs to be expressed in terms of its dependence on l, which is hidden in its dependence on n. In this respect, the energy is given by:

$$E_n = -\frac{\hbar^2}{2ma^2}\frac{1}{(j_{\max} + l + 1)^2}$$

[1] Technically the claim that this equation is true is the theorem. The wording that everyone uses just bothers me.

As I said above, we want to apply the Feynman-Hellmann theorem in the case of $\lambda = l$. So, first we'll calculate the derivative of E:

$$\frac{dE(l)}{dl} = \frac{\hbar^2}{ma^2} \frac{1}{(j_{\max} + l + 1)^3} = \frac{\hbar^2}{mn^3a^2}$$

where I have converted back from l dependence to n dependence because we no longer need the l dependence to be explicit. Next, we'll calculate the derivative of H with respect to l:

$$\frac{dH(l)}{dl} = \frac{\hbar^2}{2m} \frac{2l+1}{r^2}$$

Finally, we'll compute the expectation value of this derivative:

$$\left\langle \frac{dH(l)}{dl} \right\rangle = \frac{\hbar^2}{2m}(2l+1) \left\langle \frac{1}{r^2} \right\rangle = \frac{\hbar^2}{m} \left(l + \frac{1}{2} \right) \left\langle \frac{1}{r^2} \right\rangle$$

So, plugging our results into the Feynman-Hellmann theorem, we have:

$$\frac{\hbar^2}{mn^3a^2} = \frac{\hbar^2}{m} \left(l + \frac{1}{2} \right) \left\langle \frac{1}{r^2} \right\rangle$$

from which $\langle r^{-2} \rangle$ is very easily solved for:

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{1}{(l + \frac{1}{2})n^3a^2} \tag{13}$$