

**Subject:** Re: Calculating the spectrum of an atom

**From:** "Monk, Nicholas" <Nicholas.Monk@warwick.ac.uk>

**Date:** 23/09/2014 02:26

**To:** "Moody, John" <john.atwell.moody@gmail.com>

**CC:** "Westbury, Bruce" <Bruce.Westbury@warwick.ac.uk>, "Reid, Miles" <Miles.Reid@warwick.ac.uk>, "Sparrow, Colin" <C.Sparrow@warwick.ac.uk>, "Wood, David" <David.Wood@warwick.ac.uk>, "Jones, Timothy" <T.S.Jones@warwick.ac.uk>, "Monk, Nicholas" <Nicholas.Monk@warwick.ac.uk>

Dear All,

I think you have the wrong Nick Monk - happens sometimes!

Best,

Nick

Dr Nicholas Monk, National Teaching Fellow, Assistant Professor & Deputy Director, IATL.

On 23 Sep 2014, at 11:18, "john moody" <[john.atwell.moody@gmail.com](mailto:john.atwell.moody@gmail.com)> wrote:

On Tue, Sep 23, 2014 at 1:34 AM, john moody <[john.atwell.moody@gmail.com](mailto:john.atwell.moody@gmail.com)> wrote:

Hi Bruce, Colin and Miles,

(I'm ccing to T Jones, Nicholas Monk, Dave Wood since I mention them in this email)

Anyway this is just rambling. I guess the previous email which I wrote is maybe a sort of high water-mark of my own understanding of the existing history of the subject as far as it concerns spectra of atoms not in an external magnetic field; the kind of thing where a really strong student, if I had one, could take that broken rubbish and start to make something more reasonable out of it.

And so I am going to eventually just paste it into 'standing waves' in the end of the history section in place of mentioning Cowan's work in New Mexico, which may have included even more adventurous uses of statistics and least squares.

Then i want to think about something else, which is, many people reacted to things I put in K-12 Economics. Namely, what I noticed

1. Subsequent to my saying I liked S. Siklos solutions to past S.T.E.P. papers, these got linked to the Warwick Maths site. I don't know if it always was, or if someone thought I was right to think that some S.T.E.P. questions are unfair for some students. I know past papers can be a bad idea, but in some settings (like when a student is at a crap university and has no access to a teacher) they can help make things be fair. That is, an entrance exam is not an exam of course material.
2. Subsequent to my writing that excerpt of the student who wrote of his step father "How fucking dare you!" about giving him a mac phone instead of an android, the open learning people changed their website and put a 'technology wiki' there. Very nice, and regardless of whether it was based on my book, it was a change in a direction which I admire.

3. It appears that initially Tim wrote things sort of retracting any idea that C<sub>60</sub> is such a special compound, and then later he seems not to have so much stuff about spin-off corporations. I note he is on about 20 boards and committees, as always, but now has a sort of family of students, one might think some might be kids who would have been kicked out under uni rules otherwise, the rules I was sort of objecting to, but even if not, it is just a much nicer feeling about is online presence.

I haven't had time to really look and think about this, but one issue is, if my book was sort of scolding people, and they 'pulled their socks up,' then having my book remaining online is sort of what Americans call 'mean.'

I talked about this to someone who said, well the book is only for kids, just leave it there. But I want to anyway put something at the end saying that things got better.

And a lot of my wanting to straighten out my thinking about chemistry was because I'd gone out on a limb to talk about someone's research outside my own department, initially very emotional and critical, though, my statement at the end of the disclosure about how the university's ethics shouldn't be from the apple of his eye only, could have sounded like signing off somehow in a nice way, too.

So I will anyway cc this to the three people who may have done the 'right thing' and currently are sort of incorrectly not given credit in my book, with a promise that I will change the book when I have time, that is

Dave Wood  
Tim Jones  
Nicholas Monk

On Tue, Sep 23, 2014 at 12:34 AM, john moody <[john.atwell.moody@gmail.com](mailto:john.atwell.moody@gmail.com)> wrote:

A number of points here, which should begin to make a convergence between Hartree-Fock, Stern-Gerlach, highest weight theory, and polarization, and also the notion of a 'moving' or fixed intuition about atoms.

First, I found out why the Wikipedia description of Stern-Gerlach is wrong, that educational video incorrectly saying that a bar magnet thrown through a magnetic field will be pulled one of two directions depending on its orientation.

That was indeed a mistake in Wikipedia, in fact, Stern-Gerlach uses a *\*gradient\** magnetic field. That is the point, a gradient. This then differentially pulls the two poles of a magnet depending on the relative field strength at the two poles.

A second place a gradient magnetic field is used is in MRI imaging, and there what is measured is the RF signal which comes from Larmor precession. An interesting lemma, when you look at the classical description of Larmor precession, is that it is independent of polarization, that is, the frequency is independent of the direction of the field.

Now, a group theory lemma is this: if you define a 'polarization' to be a choice of a maximal torus and a fundamental system of positive roots, then this actually corresponds to something physical, or at least, in the Schroedinger equation solution space.

If you think about defining ocean waves by differential equations, you can say perhaps there is  $\{it\ some\}$  solution and just keep in mind the equation itself, which has all this symmetry.

Or you can say, I want to see what the actual waves look like {it now}

Now, an obvious group theory lemma is this: if you define a 'polarization' to be a choice of a maximal torus and a fundamental system of positive roots, then this can actually correspond to something physical in the Schroedinger equation solution space.

Recall that there actually is a finite-dimensional vector space of solutions associated to what is labelled an 'electron configuration,' and these are actually full solutions of the correct Schroedinger equation -- there is not technology in PDE's or numerical analysis to write these down, but they are there.

These are alternating forms, and up to isomorphism as a vector space it is just, if the 'electron configuration' is a configuration of  $k$  electrons, it is as a vector space the  $k$ 'th exterior power of the space of solutions for a single electron

Such a thing actually corresponds to a solution space of the Schroedinger equation, and this remains true regardless of whether we include electron-to-electron repulsion, or whether we include the little operators near the identity as coefficients of the potential terms  $k_{pe}^2/r_{i}$ . Because there is the perturbation which we can apply to move this solution uniquely into place, and we can even know its first derivative, so we know \*which\* schroedinger equation it is a solution to, in the sense that the constant term  $E$  of the eigenvalue, we know the constant and linear terms of it in terms of a perturbation or deformation parameter.

Although there is not one wavefunction for each polarization, once you index things by 'electron configurations,' and choose an electron configuration and a term symbol (also in the rare cases when one term symbol can occur with multiplicities, choose just one term symbol) then up to ambiguities only of a complex phase and magnitude, there is exactly one wave function that 'has' each polarization.

For these wave functions there is a possibility to have one's cake and eat it too. To have a fixed image of a standing wave, which has a variable complex coefficient. And choosing that coefficient really does describe what the field is 'now' at each point of space. That is, it determines a particular complex alternating form, up to an undefined coefficient.

Then there might be an argument for adopting as an analogy, what happens in the  $n$  body problem, in the case of a solar system like the one we happen to live in, where each planet has an elliptical orbit, and the orbits are actually in planes, and tilted at various angles.

Among general wave functions, they are just a special type, and while they cannot represent every energy level that can occur, and we might think of them as analogous to when planets go in planar orbits separately.

A polarization can be interpreted in a very easy way. For instance if one thinks of one atom as being just a set of electrons, and includes both ordinary and infinitesimal components of wave functions. For an atom with, say, three electrons, one can visualize three ordinary spheres, like three globes, and each having a very tiny sphere inside it.

Then a polarization just means marking each large sphere by one point, and marking each small sphere by one point. One can do this by placing a large 'vector' and a small 'vector' whose tail is at each electron, not caring exactly how large or small they are.

Then the space of wave functions does decompose into Fourier components, and each component has a wave function that 'has' that polarization, unique up to a choice of complex phase (including magnitude

and angle). But these components large-dimensional components are not related to energy levels.

If one begins to think the electrons are more coalesced together, then one uses a smaller symmetry group. Now it is just a single large sphere and a single small sphere. Or, choosing just one large vector and one small vector. The space of polarizations is now a cartesian product of two spheres. And again there is a unique wave function, up to complex phase and magnitude, which 'has' each polarization, within each Fourier component. And now, what was not true before is true, at least coarsely. All the wave functions in each Fourier component have the same, what is known as, coarse, energy level, and this means that for a polarization in this sense, there really is a wave function that 'has' the chosen polarization and, at least coarsely, represents each energy level.

Up until cases like an excited configuration of Nitrogen or Fluorine the coarse energy level determines the Fourier component, but this is not true generally, each Fourier component is allowed to occur more than once, with more than one coarse energy level, but usually it only occurs once.

An issue about 'spin' is that the symmetry group that is relevant for the small sphere is not just rotations of space, but this is because there is no reason for it to be that, it is symmetries of the residue of the wave function which is not a wave function in space. But it does not affect what one means by a polarization, and this detail can be ignored.

Now, if we are {it even more} accurate, we realize that the two spheres, the large sphere and the small sphere, are actually not different after all. But, the symmetry group is not just the spatial symmetry group, if you care about what you mean by a wave function, including the infinitesimal part. It is a symmetry group of a bundle of lines, and there are two symmetries that correspond to each one rotation of ordinary space. But it is a double cover of the ordinary rotation group.

When one realizes that the two spheres are not different after all, then all a polarization means is a point of a sphere, or an actual direction in space, as if you are looking at the atom itself, and the vision determines one direction into it.

And each Fourier component that corresponded to one coarse energy level (though more than one coarse energy level could correspond to a Fourier component) now splits into parts in a way that is easily understood in terms of Clebsch Gordan theory.

Again, there is a unique wave function in each of these smaller Fourier components which 'has' each polarization. And now, because the rotation group (or more correctly its double cover) really is the actual symmetry group of the atom, it really is true that there is a polarized wave function representing every possible energy level.

The reason these are useful is that if one wanted to find all the energy levels, and did not care about anything else, at any point of this analysis one can ignore all but the special wave functions that 'have' one chosen polarization.

And then, thinking of distinct Fourier component subspaces as being different, there is a bijection between the fine energy levels and the special wave functions, defined up to complex phase and magnitude, which 'have' any one fixed polarization.

So that once a polarization (single point or point of view) is fixed, each fine energy level really does determine exactly one wave function (up to phase and magnitude) and vice-versa.

Now, it is *\*not\** true that every wave function 'has' a polarization. That would be like saying every solution of the n body problem consists of planets in separate planes.

But it is true, once we are down to the smallest relevant symmetry group, that in the multiplicity free case a polarization and energy level determine a unique wave function up to a coefficient determining a complex phase and magnitude.

I think that Feynman was wrong to think that such coefficients are just intrinsically undefined, but it has to do with making a choice about what you want to see.

Now, For a general type of wave function, even if it is isotypical in the multiplicity free case, it is not true that it admits any polarization.

And this is just the assertion that Dirac was transfixed by, when he would talk about how operators are generalizations of numbers.

That is, we can visualize its representation-theoretically, and we can say there simply isn't one element or line that has been specified. That was perhaps a mysterious phenomenon in Dirac's day, but the notion of 'operator' has been replaced by the notion of the rational representation theory of Lie groups.

To reiterate, I am not asserting that an electron actually *has* such a polarization as this, defined by choosing a maximal torus and a system of positive weights, or even that one electron is separate from others in an atom.

Rather, what people say seems to happen is that the electron seems to actually orbit the nucleus just as the earth orbits the sun.

Then there might be an argument for adopting as an analogy, what happens in the n body problem, in the case of a solar system like the one we happen to live in, where each planet has an elliptical orbit, and the orbits are actually in planes, and tilted at various angles.

The sense in which it is an analogy is one which is a bit subtle perhaps, it is that we have insisted on global analytic solutions, but these were analytic on a resolution of singularities only.

Regarding the fine structure, the supposed 'spin-momentum coupling' is described as requiring adding a term to the Laplacian, equivalent to multiplying the potential term  $Ze^2/r$  term by an operator coefficient near the identity

$$(1 + 1/(4m^2c^2))[C_{\Delta} - C_1 - C_2].$$

with  $C_i$  the Casimirs. This is *almost* equal to the much more believable  $1 + 2(\hbar/(2\pi))^2(1/(2m))$   
 $(1/\hbar)(1/(4\pi\epsilon_0))^2(1/\hbar)[C_{\Delta} - C_1]$

which just corresponds to having used the correct Laplacian in the first place (including its action on first principal parts. And anyway, the group  $SO_3 \times SU_2$  or its cover  $SU_2 \times SU_2$  occurs *naturally* as automorphisms of the first principal parts of a naturally occurring  $O(-1)$  on the Riemann sphere.

Here is where the issue of polarization enters the picture. The expressions  $C_{\Delta}$ ,  $C_1$ ,  $C_2$  are Casimirs of subgroups of the huge group which is

$$(SU_2 \times O_3)^k$$

If we have chosen a maximal torus for the  $SU_2 \times O_3$  that relates to just the three subgroups which

are 1 in all but the  $k$ 'th place, and either  $SU_1 \times 1, 1 \times O_3$ , or the diagonal  $SU_2$  in the  $k$ 'th place.

And if we have chosen a maximal torus and also a fundamental system of positive roots, then there is a unique highest weight vector for each irreducible component in the decomposition of our larger space of wave functions (the exterior power) as a representation of that subgroup which is 1 in all but the  $k$ 'th factor and  $SU_2 \times SO_3$  in the  $k$ 'th factor.

That is, a unique line, and because it is highest weight simultaneously in three different senses (as a representation of any one of the three subgroups), it actually is then isotypical for all three actions, and this means that each of  $C_\Delta, C_1, C_2$  just acts by a number.

The importance of this is that by specifying all three numbers and also specifying the number which says how the diagonal torus acts, you are intersecting four lattices in an integer lattice whose rank is the dimension of the vector space corresponding to the electron configuration. In the multiplicity free case, the usual case, this is just an infinite cyclic group, and a generator of this group is  $\{it\}$  nearly, but not quite, an eigenvector for the whole operator. If the operator is restricted in the least squares sense, the action is a very good approximation of what is called the energy level (the number such that differences of two give the frequency correction).

And in the case of multiplicities within an electron configuration, it is very easy to just consider the least squares restricted action to be by a small matrix (a two-by-two matrix in case of a multiplicity two term symbol in one electron configuration) and to use the eigenvalues of that, easily determined.

The inaccuracy with this interpretation is down to the fact that a basis of the homogeneous harmonic polynomials is chosen using Legendre's lowering operator, whereas the representation theory is based on Weyl's lowering operator. They differ just by a coefficient which can be given a multipole expansion, but it is not compatible with a perturbation approach since multiplying a harmonic basic function (times a Schroedinger radial function) by this coefficient transports it into an orthogonal Hilbert space, and also there are issues of convergence, and issue of imaginary numbers, such as whether a series  $\sqrt{r^2/z^2-1}$  should be expanded  $\{it\}$  about the imaginary square root of -1. This seems wrong, but the current approach that is used is equivalent to taking the first term in such a series, taking the constant term to be imaginary. The perturbation matrix (which is Hermitian) ends up having real entries when this is done, so there is no issue about real versus imaginary. Also the integrals of  $r^2/z^2$  do end up converging, but only for low powers I think. And finally that the resulting perturbation is zero.

This difficulty is really insoluble, because it comes down to the fact that a finite-dimensional Lie group interpretation really cannot make sense. If one thinks about it, it is here an approach based on considering first principal parts. There is no reason not to consider higher principal parts, but in the end one is going to have to have a theory which is not centered on a perspective at the center of mass of a single atom anyway.

It is maybe best to consider the errors in the current approach as signifying a fundamental gap between the local Weyl perspective and the more global Legendre perspective. One is pretending that one single finite-dimensional vector space has meaning with respect to global harmonic functions, and also with respect to Weyl's complex lowering operator, when clearly there is really a distant analogy, an analogy one might say between the visions of two thinkers, who tried to come to a common understanding, but knowing it is very temporary, transient.

The 'current' of an electron is said to be the number of times it orbits the nucleus per second, and the 'magnetic moment' is the product of this with the surface area contained in that loop. Then this moment, by taking a 'cross product' with a 'magnetic field'  $B$ , results a torque, meaning, a value of the time derivative of the 'angular momentum vector.' Projecting this 'vector' to a plane perpendicular to the

direction of  $\mathbf{B}$  amounts to dividing by its magnitude and the sin of the angle, but the cross product amounts to multiplying by these same two quantities, and the result is that the angular velocity of the angular momentum vector is the product of the magnitudes of the magnetic moment, and the magnetic field strength, divided by the magnitude of the angular momentum.

The sense in which it is an analogy is one which is a bit subtle perhaps, it is that we have insisted on global analytic solutions, but these were analytic on a resolution of singularities only.

Another thing I want to say here is, in this whole analysis, we have *\*first\** taken global sections, and *\*then\** taken a tensor product, and that is in a situation where that was OK as the relevant line bundle is very ample.

But a very important thing to think about is, was the reason for setting up this whole picture this way, that people started out wanting global solutions working globally, and so when one says 'indecomposable tensor' one cannot think of anything but a product of two global sections?

One issue is that the group  $SU_2 \times SO_3$  really should be viewed as a local automorphism group, where the  $SU_2$  factor might not integrate to a group at all.

That is, all the calculations here are in some sense trivial in a way that is unfamiliar to me, in the sense that all the algebraic geometry is uninteresting.

Yet, to be a bit blunt about people like Dirac, that is a necessary consequence of approaching the subject from a standpoint when one cannot understand things like nontrivial line bundles.

If you really look at how the subject is done, a physicist will read a few papers, and then come up with his theory. But it is a theory like a badly naive undergraduate would have come up with. And the history of it is the say "Well, what does any *\*respectable\** theory need to have. It has to have an energy-momentum tensor, so here is an energy-momentum tensor..."

And then always they work in a setting where all line bundles are ample etc etc.

Perhaps one reason I still have not got the infinitesimal part right is that I'm just trying to match the vector space picture these guys already present.

Yet I'm pleased to have read Condon's statement that for more than one electron they never got that to work, and it really is time for someone, perhaps a student, to start fresh and find a more believable description.

It was unfortunate too that Feynman got lumbered with having to carry a Spinor theory interpretation around in his pocket, as a result of the failure of anyone to have done this, the failure of any student of algebraic geometry to have started looking at Schroedinger's paper.

... a couple of other points. When I refer to an integral that doesn't converge, this is in calculating the action of  $C_\Delta, C_1, C_2$ , so it only affects the fine structure. Condon says it only affects type s orbitals, but that is wrong, there is one term in a sum that is just a divergent integral. It has to do with how making the Casimir dimensionless requires dividing by  $r_i^2 = x_i^2 + y_i^2 + z_i^2$ .

In regards the Zeeman lines, so far I have not really said anything about what happens in a magnetic field, but one thing is that there is yet another factor of 2 that is introduced for no reason at all.

That is, when people say that there is 'spin angular momentum' using a particular operator  $S$  whose square

is the Casimir of  $SU_1 \times 1$ , it turns out not to be the eigenvalue of  $S$  that enters into the Zeeman shift, as it is the eigenvalue of  $L$ . Rather, it is necessary, for no reason in the world, to double this eigenvalue.

This doubling of the eigenvalue of the  $S$  operator may relate to the double covering map  $SU_2 \rightarrow SO_3$  somehow, but it makes sense to have a correct theory that explains the spectrum of atoms when not put into artificial magnetic fields in the first instance. So there are these very dodgy numbers like 2 for the gyromagnetic ratio for spin, and  $1/2$  for the "Thomas half," and the  $1/4$  in the expression  $(1 + 1/4[\dots])$ , and they are put in with no explanation.

I forgot to say something else, which is related to this: subsequent to my having suggested in K-12 economics, students looking at the relations between 3 branches (crystal symmetry, photovoltaic effect, energy use), I did notice actual work on those things exactly (some by Tim and his students) including thinking about actual crystal solids that exist in 3 space.

So, part of my feeling a little responsible to sort these things out is, I had said initially sort of boasting about how  $C_{60}$  has a simple symmetry group (which, for no particular reason, the chemists who synthesized it has acting freely and transitively on the Carbon atoms too by the way!), and then said, well this should not be taken as advice for a student as the road of needing to consider the next and the next is a standard funding lie for Maths.

But at the same time I'm aware that people are doing similar stuff about actual crystals in 3 space, and photovoltaic, and making integrated chips and crystals perhaps, and also relating this to notions of electron spin.

And the reason they are doing this certainly is how electron spin is something that seems to defy intentionality, it is in the 'quantum computing' ideas, as defective as these appear to me to be.

So I sort of felt to help keep up with this effort here, to try to look at this issue, and I have not resolved it, but one way of thinking about what it is, is that like when a complex function has a pole, there is a residue which is a number.

Now, the electrical potential has a pole, but people would usually say the electron never goes there. Yet, if you try to work analytically, then you are working implicitly on a resolution of singularities, analogous to polar coordinates in the plane when the square root of  $x^2+y^2$  is included as an analytic coordinate, but there on the exceptional divisor is where the 'residue' becomes something quite a lot like an infinitesimal version of the wave function you started with.

So there is locally sort of a pair of wave functions to consider, one which might be considered to be somehow infinitesimal.

Maybe people don't always think of complex residues as being infinitesimal. Some of my y2 students wanted to connect something I was saying about cotangent bundles to magnetism; about how any surface in a cotangent bundle has a natural flux through it, if it is oriented, a number. A notion of a tangent or cotangent bundle can sometimes be thought of as being infinitesimal, like a space of velocity vectors is sometimes visualized as infinitesimally small, a neighborhood of a point.

So it is not that anything is spinning, but that there is a second order of accuracy that needs to be considered when you allow potential functions which have a pole, and yet also there is a geometric way of understanding the pole in terms of a winding number too.



