

Some basic computational aspects of chemistry.

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Abstract

A new mathematical formalism is developed to discuss chemical bounds in an appropriate graphical way.

1 Introduction.

Chemistry is about mutations between stable systems where stability refers to approximate eigenvectors of the Hamiltonian at hand. Usually, the nucleus is treated classically given that its quantal aspects are four orders of magnitude below the lowest average radius for the average distance of an electron to the nucleus, which of the order of an Angstrom. Hence, given that chemical reactions concern processes taking places in the outer electron layers, such details are totally insignificant. In this semiclassical nonrelativistic approximation, it is utterly clear that the wave function cannot exactly solved for as multi electron interaction cause shifts in the energy levels of the one electron Hamiltonian defined by an electron moving in the electrostatic potential of the nucleus. Effects resort under the Zeeman spin splitting effect where an energy level gets a spin correction or Balmer lines where a continuum of eigenstates develops due to the repulsive electron-electron interaction.

The aim of this paper is to develop an alternative formalism mapping to the multiparticle wavefunction formalism which allows for an easy visualization of the physics behind atomic and molecular binding. In general, start from a one particle Schrodinger equation

$$i\partial_t\Psi = -\frac{1}{M}\Delta\Psi - \frac{Ne^2}{|\vec{r}|}$$

where we have put $\hbar = 1$ and N equals the number of protons in the nucleus. Gravitational corrections are momentarily not considered and neglected. Fortunately, such equations can be solved exactly but the more complicated problem with multiple electrons can't due to the electron-electron interaction terms. In this case, it is necessary to resort to a Feynman series expansion for scattering processes on a fixed potential, without change of particle number, and smear out with a wave function such that the left hand side equals the right hand up to a constant unitary number. It is clear that stable eigensolutions to this

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problem are uniquely characterized by the geometry of space of solutions to the equation

$$\nabla |\Psi(t, r, \theta, \phi)|^2 = 0$$

which are the optimal places where the particle should reside. In ordinary flat space, this place is given by a circle due to rotational symmetry given that a rotation is characterized by an axis. In a general curved space, this argument will not hold in the original quantum theory but it does in the one developed by this author in a special case, given that infinitesimally, everything reduces to flat three spatial dimensions. In the latter case, the problem allows for a separation of variables $\Psi(t, r, \theta, \phi) = R(t, r)S(\theta, \phi)$ and by choice of the z axis as rotation axis,

$$S(\theta, \phi) = e^{im\phi} S_j(\theta)$$

with $-j \leq m \leq j$ and $2j \in \mathbb{N}$.

2 Semiclassical treatment of one particle wave function.

We shall treat the previous problem from a heuristic, semiclassical viewpoint using some well known theorems from group representation theory. All known irreducible representations of $SU(2)$ with generators L_k satisfying

$$[L_j, L_k] = i\epsilon_{jkl} L_l$$

are given by an half integer positive number j , $m = -j, -j+1, -j+2, \dots, j-2, j-1, j$ and states $|j, m\rangle$. Traditionally, one defines the operator

$$A = L_1 + iL_2$$

satisfying

$$A^\dagger A = L_1^2 + L_2^2 - i[L_2, L_1], AA^\dagger = L_1^2 + L_2^2 + i[L_2, L_1]$$

and therefore

$$A^\dagger A + AA^\dagger = 2(L_1^2 + L_2^2), AA^\dagger - A^\dagger A = -2L_3.$$

In matrix language

$$A^\dagger |j, m\rangle = \sqrt{(j-m)(j+m+1)} |j, m+1\rangle$$

and

$$A |j, m\rangle = \sqrt{(j-m+1)(j+m)} |j, m-1\rangle.$$

In quantum physics, we know very well the Peter-Weyl theorem which states that the correct representation we have to deal with is given by

$$\oplus_{j=0}^{\infty} (2j+1) H_j$$

where H_j is the representation space of spin j and the multiplicity of occurrence equals its dimensionality.

We notice now that the geometric place attached to the condition

$$\nabla |\Psi(t, r, \theta, \phi)|^2 = 0$$

is a rigid string; given that the gradient reads

$$\nabla = \partial_r \otimes \partial_r + \frac{1}{r^2} \partial_\theta \otimes \partial_\theta + \frac{1}{r^2 \sin^2(\theta)} \partial_\phi \otimes \partial_\phi$$

we obtain that the space orthogonal to it is spanned by the vectors

$$\partial_\phi, \partial_\theta |\Psi(t, r, \theta, \phi)|^2 \partial_r - \partial_r |\Psi(t, r, \theta, \phi)|^2 \partial_\theta$$

which has a rather complicated dependency upon $|\Psi(t, r, \theta, \phi)|^2$. At the critical circle, the gradient vanishes and the orthogonal space becomes the entire three space spanned by $\partial_r, \frac{1}{r} \partial_\theta$ and $\frac{1}{r \sin(\theta)} \partial_\phi$.

Here, the Hessian

$$H_{ij} = \partial_i \partial_j |\Psi(t, r, \theta, \phi)|^2$$

is a symmetric tensor at the critical points with signature $(0, -, -)$ due to the maximal character of the local density. Geometrically the trace $g^{ij} H_{ij} < 0$ as well as $g^{ik} g^{jl} H_{ij} H_{kl} > 0$ fully characterize the spectral properties of H_{ij} . Notice that in a more limited covariant sense, by going over to coordinate systems adapted to the metric at critical points, three eigenvectors also become distinguished; those vectors, as well as the above two invariants are all θ independent in flat three Euclidean geometry. The eigenvalues $\lambda, \mu < 0$ of $H_{ij}(x)$ in coordinate systems where $g_{ij}(x) = \delta_{ij}$ determine ‘‘curvature’’ radii with

$$g^{ij} H_{ij} = \lambda + \mu, g^{ik} g^{jl} H_{ij} H_{kl} = \lambda^2 + \mu^2.$$

One can also speak about the *intrinsic* curvature of the induced metric on the level surface and that definition differs from the previous one given that it does not take into account the fluctuations of $|\Psi(t, r, \theta, \phi)|^2$. There are two natural length scales associated with the string without knowing the wave function; those are the lengths of the vectors $r \partial_r, \partial_\theta$ namely

$$r_\star = r, r_\star = \sqrt{g(\partial_\theta, \partial_\theta)}, r_\star = \sqrt{g(\partial_\phi, \partial_\phi)}.$$

This intrinsic geometry approach offers less information as it gives only one length scale given that any two dimensional space is an Einstein space.

In a spin one representation,

$$L_1 = i(\cos(\phi) \partial_\theta - \sin(\phi) \partial_\phi), L_2 = i(\sin(\phi) \partial_\theta + \cos(\phi) \partial_\phi), L_3 = i \partial_\phi.$$

Therefore,

$$\partial_\theta = -i(\cos(\phi) L_1 + \sin(\phi) L_2) = -\frac{i}{2} (\cos(\phi)(A + A^\dagger) - i \sin(\phi)(A - A^\dagger))$$

which can be rewritten as

$$\partial_\theta = -\frac{i}{2} (e^{-i\phi} A + e^{i\phi} A^\dagger).$$

Therefore,

$$r_\star = \sqrt{g(\partial_\theta, \partial_\theta)} = r \sqrt{\frac{\text{Tr}(A^\dagger A)}{2}} = \frac{r \sqrt{(2j+1)j(j+1)}}{\sqrt{3}}$$

because $\text{Tr}(A^2) = 0$ and the cyclic property of the trace or

$$r_\star = r \sqrt{\frac{\langle j, m | A^\dagger A + A A^\dagger | j, m \rangle}{4}} = \frac{r \sqrt{j(j+1) - m^2}}{\sqrt{2}}$$

because the diagonal elements of A^2 vanish. Finally, the other r_\star equals $r_\star = r \sin(\theta)m$, rm by means of a similar replacement

$$d\phi \otimes d\phi(\partial_\phi, \partial_\phi) = \langle j, m | L_3^2 | j, m \rangle.$$

The picture we have in mind now is that of a rotating string at a distance r and angular momentum $\hbar m$ leading to

$$M(r \sin(\theta))^2 \dot{\phi} = \hbar |m|.$$

On the other hand, we have found two relevant length scales at this string r , $\frac{r \sqrt{j(j+1) - m^2}}{\sqrt{2}}$ associated to directions perpendicular to the string tangent. Given that $\sin(\theta)$ is dimensionless and we have one natural dimensionless number satisfying all requirements, it is natural to posit that

$$\sin(\theta) = \frac{\sqrt{j(j+1) - m^2}}{\sqrt{j(j+1)}}$$

and therefore

$$\dot{\phi} = \frac{\hbar |m| j(j+1)}{Mr^2(j(j+1) - m^2)}$$

which might be a useful inverse timescale. It has to be understood that those length scales can be associated to pressures which must match an energy density when the wave function is associated to a perfect fluid. Obviously, this pressure is not isobaric given that rotation occurs and therefore ∂_r must be an exception. Therefore, given that the energy density of an elementary unit length $\delta l = r \sin(\theta) \delta\phi$ element on the string is given by

$$\left(\frac{\hbar^2 m^2}{4\pi Mr} - \frac{Ne^2}{2\pi r} \right) \delta\phi.$$

Assuming the string has a string tension, an internal energy due to tension should be added; the natural one being

$$\hbar \dot{\phi} = \frac{\hbar^2 |m| j(j+1)}{Mr^2(j(j+1) - m^2)}$$

resulting in the balance

$$\frac{Ne^2}{r^2} = \frac{2\hbar^2 |m| j(j+1)}{Mr^3(j(j+1) - m^2)}$$

because the kinetical energy associated to any string element vanishes when the latter is seen as a homogeneous infinitesimally thickened charged fluid string. Ignoring the electrostatic fluid selfinteraction, this results in

$$r = \frac{2\hbar^2 |m| j(j+1)}{MNe^2(j(j+1) - m^2)}.$$

Regarding the average distance in the plane to the origin, it suffices to take the semiclassical treatment

$$\frac{L^2}{Mr^3} = \frac{Ne^2}{r^2}$$

resulting in

$$r = \frac{\hbar^2 j(j+1)}{MNe^2}$$

which is one half of the $j = m$ limit of our previous formula. This suggests a similarity between the “pole values” ($m = \pm j$) and the average value estimated before which is m independent. It is to be noted that our string radius grows with m and j and that the previous formula for the average radius only holds for large m, j and receives otherwise $\frac{1}{|m|}$ corrections.

It is kind of self evident, from semiclassical approximations, that the leading order contributions to chemical reactions will occur at the critical and not “average” string given that densities would have to multiply and a law of large numbers occurs provided exponential falloff of the density occurs near the critical string which is the case. This implies that deep atomic penetration at the order of an Angstrom or just one order above is required for realistic chemical interactions to take place.

3 The atom and spin corrections to string radii and oscillations.

Through experiment, one knows that electrons carry an extra internal spin $\frac{1}{2}$, a feature which distinguishes a preferred rotational axis which is the one associated to the direction of the spinning particle. Given that spin $\frac{1}{2}$ -particles are fermions, which means their wave function is anti-symmetric, it follows that two fermions in the same $|k, j, m\rangle$, where $k = 1 \dots 2j + 1$, spatial quantum state have anti-correlated spins

$$|\uparrow\rangle \otimes |\downarrow\rangle - |\downarrow\rangle \otimes |\uparrow\rangle.$$

Hence, a spin- $\frac{1}{2}$ pair in the same spatial quantum state provides for no direction in spin space anymore and behaves effectively as a spin zero boson. Obviously, there can be no three fermions in the same $|k, l, m\rangle$ state since spin- $\frac{1}{2}$ space is two dimensional. Nevertheless spin coupling to the electromagnetic field of the nucleus as well as electron-electron interactions cause the energy levels and therefore spin radii to shift.

So, a first approximation consists in taking the Hartree Fock approximation where the wave function can be written as

$$|\Psi\rangle = \otimes_{k,j,m,s} |r(j, m, N, e^2, M), \theta(j, m); s\rangle$$

with antisymmetrization over s in case k, j, m are identical and symmetrization over s “pairs” in case the particles are deemed to be indistinguishable. To couple electromagnetism to classical spin, we need a vector potential given that we need a timescale to join the operator $\hbar\vec{\sigma}$ where the latter is the vector consisting out

of Pauli matrices. The Coulomb energy is a scalar; therefore, it cannot serve for these purposes. Vibrations of the nucleus will cause electromagnetic waves to form with a direction in space breaking up the spin pairing and causing for the energy levels to oscillate in a spin dependent way. Remains to consider the electron-electron pairing which is effectively modelled between spinless double strings in case both s -levels are filled up.

Electron-electron interactions are modelled by...

4 Chemical bounds between atoms.