

# AO BASIS SETS AND MANY-PARTICLE WAVE FUNCTION

MATTHEW R. HENNEFARTH

## 1. ATOMIC ORBITALS BASIS SETS

In general, our molecular orbitals  $|\phi_p\rangle$  are expanded in terms of some atomic orbitals  $|\phi_\mu\rangle$ . One could use some atomic orbitals which are solutions to the single nuclei-single electron problem. However, this would only be qualitatively correct. The single-particle orbitals would not have any electron-electron interaction in them. Instead, what if each atomic orbital is approximated as some linear combination of Gaussian function? This would on one hand yield nice integrals which we could compute fast, and allow us some flexibility in building our basis set. The reason we also choose a linear combination of Gaussians is that for higher AO's, like the 2s, we have a radial node which could never properly be described by a single Gaussian. In general, our AO's are typically contracted Gaussian-type orbitals and take the form

$$\phi_\mu(\mathbf{r}) = Y_{lm}(\theta, \varphi) \left( r^l \sum_{i=1}^n c_i \mathcal{N}(l, \alpha_i) e^{-\alpha_i r^2} \right) \quad (1)$$

In the above,  $n$  is the number of contracted primitive Gaussians,  $Y_{lm}$  is a spherical harmonic,  $c_i$  is the contraction coefficient, and  $\alpha_i$  is the corresponding exponent.  $\mathcal{N}$  is just a normalization factor such that  $\langle \phi_\mu | \phi_\mu \rangle = 1$ . For a given basis set, all of these parameters are fixed such that one only is trying to optimize instead the transformation matrix from AOs to MOs,  $\mathbf{C}$ . One can of course explore the various basis sets used in quantum chemistry at the Basis Set Exchange [3, 1, 4].

**Example 1** (STO-3G Basis for Hydrogen). From the Basis Set Exchange, one can see that the STO-3G basis set [2] for a hydrogen atom is given by Table 1. We form a single 1s orbital from three primitive Gaussian-type orbitals. The contraction coefficients and exponential terms  $\alpha$  can be plugged into Eq. (1).

The one drawback of using Gaussian type integrals is that they do not correctly model the cusp-condition at the nuclei. Of course, contraction scheme can only approximately

---

*Date:* March 21, 2024.

TABLE 1. STO-3G Basis Set for Hydrogen. One contracted Gaussian-type orbital is formed from three primitive Gaussian-type orbitals.

Orbital	$\alpha$	Contraction Coefficient
1s	3.4252509140	0.1543289673
	0.6239137298	0.5353281423
	0.1688554040	0.4446345422

model this, and the Gaussian-type orbitals will always be differentiable at  $r = 0$ , unlike a Slater type orbital ( $e^{-\zeta r}$ ). Slater-type orbitals would better approximate the cusp condition; however, they are typically never used in practice due to the increase in cost to evaluate the integrals.

1.0.1. *Building AO Basis Sets.* To build an AO basis set for a particular atom, one considers some number of contractions for each orbital. Lets take the carbon atom. For a smaller basis set, we might only consider defining a 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> atomic orbital since there are no electrons in the d-shell. One would then determine how each orbital is expanded in terms of some number of primitive Gaussian-type orbitals. Then, they would (using techniques later in the course), optimize the energy with respect to the parameters (typically  $\alpha_i$  and  $c_i$ ) for each orbital. However, as it customary, all orbitals of the same shell typically will have the same  $\alpha_i$  and only vary in their contraction coefficients.

In essence, the basis sets are essentially a variational optimization of the single atom atomic orbitals given some trial wave function. One could always include more orbitals (have multiple orbitals for each valence orbital), or include higher principle orbitals (3s, 3p for carbon for example). This would yield a different basis set, and probably a more accurate trial wave function for which to build off of.

1.0.2. *Understanding Basis Set Names.* The simplest basis sets are those of the STO- $n$ G type. The STO stands for Slater Type Orbital and the  $n$ G describes the number of Gaussians used. For example, the STO-3G is the minimal basis for which each atomic orbitals is described by a contraction of 3 primitive Gaussians. In the case of Hydrogen (Table 1), we see that the 1s orbital is described by a contraction of 3 primitive Gaussians. Similarly for the carbon atom: the 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub>, and 2p<sub>z</sub> are described by 3 primitive type Gaussians. If one used instead the STO-4G, then then all atomic orbitals would be described by a contraction of 4 Gaussians! This should get us a step (albeit a small step) closer to the basis set limit result!

In practice one rarely uses the STO- $n$ G basis sets anymore for production calculations since they are so primitive. Instead, chemists have an absolute plethora of basis sets to choose from. One particularly set of basis sets are called the Pople basis sets. These are typically denoted as  $X - YZG$  basis sets. Here,  $X$  denotes the number of primitive Gaussians describing the core orbitals. The  $Y$  and  $Z$  indicate that the valence orbitals are modeled by 2 basis functions each. The first is composed of  $Y$  primitive Gaussians, and the second is composed of  $Z$  primitive Gaussians. In this particular case, we call this a split-valence double-zeta basis set. One could of course model the valence orbitals with more basis functions in a split-valence triple- or split-valence quadruple-zeta (or even higher) denoted as  $X - YZWG$  and  $X - YZVVG$  respectively.

Lets take the 3 - 21G basis set as an example; and furthermore, lets look at both hydrogen and carbon again (Table 2). The hydrogen has no core orbitals, only the valence 1s orbitals. So we model it using 2 contracted Gaussians, the first being comprised of 2 primitives and the other comprised of 1 primitive. For the carbon atom, a similar story is for the valence orbitals (note that the  $\alpha$  value is the same for both 2s and 2p!). The 1s orbitals is the core orbital for carbon and this is described by a contraction of 3 primitive type Gaussians.

One could of course go to larger and larger basis sets, 4-31G, 6-31G, 6-311G, etc. And one could also begin to add some flexibility to our basis sets with the addition of polarized

TABLE 2. 3-21G basis set for hydrogen and carbon. Note that the core orbital of carbon is modeled by a contraction of 3 Gaussians. The valence orbitals are modeled by 2 sets of contracted Gaussians, the first is comprised of 2 primitives and the second of just 1 primitive.

Atom	Orbital	$\alpha$	Contraction Coefficient
H	1s	5.4471780000	0.1562849787
		0.8245472400	0.9046908767
	1s	0.1831915800	1.0000000000
C	1s	172.2560000000	0.0617669073
		25.9109000000	0.3587940429
		5.5333500000	0.7007130837
	2s	3.6649800000	-0.3958951621
		0.7705450000	1.2158343560
	2p	3.6649800000	0.2364599466
		0.7705450000	0.8606188057
	2s	0.1958570000	1.0000000000
	2p	0.1958570000	1.0000000000

and diffuse functions (denoted as \* and + respectively). The diffuse functions are added to better model the tail portion of the atomic orbital (far away from the nucleus). Polarized functions add the next angular momentum to the given atom to give it more flexibility in describing the molecular orbital. For the case of carbon, the polarized functions would be the d orbitals.

## 2. MANY-PARTICLE WAVE FUNCTIONS

Up until this point, we have really only discussed single particle wave functions. If we want to be able to solve the electronic Hamiltonian for many-electron systems, we have to understand the formalism of quantum mechanics with multiple particles. Fortunately, the machinery is not too dis-similar from a single particle system; however, some care has to be taken with regards to particles with spin.

**2.1. Systems with  $N$  Degrees of Freedom.** Lets consider a system with  $N$  particles. Classically, we could describe this using  $(x_i, p_i)$  for  $i = 1, \dots, N$ . Just like we would do with a single particle, we can quantize this system by promoting the variables to quantum operators  $\hat{X}_i, \hat{P}_i$  such that they obey the canonical commutation relations:

$$[\hat{X}_i, \hat{P}_j] = i\hbar\delta_{ij} \quad (2a)$$

$$[\hat{X}_i, \hat{X}_j] = 0 \quad (2b)$$

$$[\hat{P}_i, \hat{P}_j] = 0 \quad (2c)$$

Since the position operators commute, we can find a simultaneous eigenbasis

$$|x_1 \dots x_N\rangle = |x_1\rangle \otimes \dots \otimes |x_N\rangle \quad (3)$$

with normalization

$$\langle x'_1 \dots x'_N | x_1 \dots x_N \rangle = \prod_{i=1}^N \delta(x_i - x'_i) \quad (4)$$

The position-space wave function is hence

$$\Psi(x_1, \dots, x_N) = \langle x_1 \dots x_N | \Psi \rangle \quad (5)$$

We may also interpret

$$P(x_1, \dots, x_N) = |\langle x_1 \dots x_N | \Psi \rangle|^2 \quad (6)$$

to be the absolute probability density for catching particle  $i$  near  $x_i$ .

In general, we identify an  $N$ -particle wave function  $|\Psi\rangle$  in the product space

$$\bigotimes_{i=1}^N \mathcal{H}_i \quad (7)$$

where  $\mathcal{H}_i$  is the Hilbert space for the  $i$ th particle. Additionally, we can promote single particle operators  $\hat{O}_i$  to this product space by

$$\hat{O}_i \rightarrow \mathbb{1}_1 \otimes \dots \otimes \mathbb{1}_{i-1} \otimes \hat{O}_i \otimes \mathbb{1}_{i+1} \otimes \dots \otimes \mathbb{1}_N \quad (8)$$

2.1.1. *Two-Particle State Vector.* We consider a 2-particle system. The state vector of this system must be some element of

$$\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2 \quad (9)$$

The Hamiltonian will take the form

$$\hat{H} = \frac{\hat{\mathbf{P}}_1^2}{2m_1} + \frac{\hat{\mathbf{P}}_2^2}{2m_2} + V(\hat{\mathbf{X}}_1, \hat{\mathbf{X}}_2) \quad (10)$$

There are two classes of problems:

(1)  $\hat{H}$  is separable, ie.,

$$\hat{H} = \frac{\hat{\mathbf{P}}_1^2}{2m_1} + V_1(\hat{\mathbf{X}}_1) + \frac{\hat{\mathbf{P}}_2^2}{2m_2} + V_2(\hat{\mathbf{X}}_2) = \hat{H}_1 + \hat{H}_2 \quad (11)$$

(2)  $\hat{H}$  is not separable, ie

$$V(\hat{\mathbf{X}}_1, \hat{\mathbf{X}}_2) \neq V_1(\hat{\mathbf{X}}_1) + V_2(\hat{\mathbf{X}}_2) \quad (12)$$

In the first case, the particles both interact with some external potential but not with each other. The second case has no restriction and the many electron problem is non-separable. While the non-separable Hamiltonians seem hopelessly hard, let's at least consider the separable Hamiltonians. Now, since  $[\hat{H}_1, \hat{H}_2] = 0$ , we can find a simultaneous eigenbasis which we will call  $|E_1\rangle|E_2\rangle$ .

$$\hat{H}_1 |E_1\rangle = E_1 |E_1\rangle \quad (13)$$

$$\hat{H}_2 |E_2\rangle = E_2 |E_2\rangle \quad (14)$$

This state corresponds to particle 1 being in energy eigenstate  $|E_1\rangle$  and particle 2 being in energy eigenstate  $|E_2\rangle$ . Furthermore, we can see that

$$\hat{H} |E_1\rangle|E_2\rangle = (\hat{H}_1 + \hat{H}_2) |E_1\rangle|E_2\rangle = (E_1 + E_2) |E_1\rangle|E_2\rangle \quad (15)$$

and hence they are the eigenstates of  $\hat{H}$ .

What do they look like in the coordinate representation? Well, we have that

$$\psi_E(x_1, x_2) = \langle x_1, x_2 | E_1, E_2 \rangle = \psi_{E_1}(x_1) \psi_{E_2}(x_2) \quad (16)$$

And in fact,  $\psi_{E_i}$  are the solutions to the single particle Hamiltonian!

### 3. SPIN

In quantum mechanics, particles are known to have an additional “orientation”, or an intrinsic property, known as spin. In general, if given a rotation,  $\Omega$ , we typically assume only the particles position will undergo a rotation as

$$\Psi(\mathbf{x}) \rightarrow \Psi(\Omega\mathbf{x}) \quad (17)$$

However, it is also possible that the wave function also transforms.

$$\Psi(\mathbf{x}) \rightarrow \Omega\Psi(\Omega\mathbf{x}) \quad (18)$$

If so, we say that the particle for which it describes has spin, otherwise we say it doesn't have spin. This is in general analogous to the vector potential in classical electricity and magnetism. Here, we only review some elementary aspects of spin for a single particle. A detailed discussion on spin and angular momentum can be found elsewhere. Then, we discuss spin for multi-particle wave functions as well as spin-statistics.

**3.1. Brief Review of Spin for Single Particles.** Particles can have spin  $0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ . There are also 3 spin operators,  $\hat{S}_x, \hat{S}_y, \hat{S}_z$  which satisfy the angular momentum algebra

$$[\hat{S}_i, \hat{S}_j] = \epsilon_{ijk} i\hbar \hat{S}_k \quad (19)$$

$$[\hat{S}_i, \hat{S}^2] = 0 \quad (20)$$

$$\hat{S}^2 = \sum_i \hat{S}_i^2 \quad (21)$$

Because of the last relation, we can find an simultaneous eigenbasis of  $\hat{S}^2$  and only one  $\hat{S}_i$ , which we typically take to be  $\hat{S}_z$ . We label these states  $|s, m_s\rangle$  such that

$$\hat{S}^2 |s, m_s\rangle = s(s+1)\hbar^2 |s, m_s\rangle \quad (22)$$

$$\hat{S}_z |s, m_s\rangle = m_s \hbar |s, m_s\rangle \quad (23)$$

Recall that  $m_s$  can be  $-s, -s+1, \dots, s-1, s$  ( $2s+1$  possible values). Finally, there are some particular interesting operators  $\hat{S}_\pm$  which raise and lower  $m_s$  by 1.

$$\hat{S}_\pm = \hat{S}_x \pm i\hat{S}_y \quad (24)$$

$$\hat{S}_\pm |s, m_s\rangle = c_\pm(s, m_s) |s, m_s \pm 1\rangle \quad (25)$$

$$c_\pm(s, m_s) = \hbar \sqrt{(s \mp m_s)(s \pm m_s + 1)} \quad (26)$$

If  $m_s \pm 1$  is outside the allowed range, the result is zero. Using the ladder operators, we can write  $\hat{S}^2$  as

$$\begin{aligned} \hat{S}^2 &= \hat{S}_+ \hat{S}_- - \hat{S}_z + \hat{S}_z^2 \\ &= \hat{S}_- \hat{S}_+ + \hat{S}_z + \hat{S}_z^2 \end{aligned} \quad (27)$$

**Example 2.** The spin-1/2 particle is particularly interesting for a variety of reasons. For us, it is because electrons are spin 1/2 particles. We often denote states as

$$|\alpha\rangle = |\uparrow\rangle = \left| \frac{1}{2}, \frac{1}{2} \right\rangle \quad (28a)$$

$$|\beta\rangle = |\downarrow\rangle = \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \quad (28b)$$

Furthermore, the operators  $\hat{S}_i$ , expressed in this basis, are the same as the Pauli matrices ( $\sigma_i$ ) multiplied by  $\frac{\hbar}{2}$ .

$$\hat{S}_i = \frac{\hbar}{2} \sigma_i \quad (29)$$

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad (30a)$$

$$\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad (30b)$$

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (30c)$$

Lastly, we denote the spin coordinate of a particle as  $\omega$  such that  $\mathbf{x} = (\mathbf{r}, \omega)$ . Hence, for spin 1/2 particles,

$$\langle \omega | \alpha \rangle = \alpha(\omega) \quad (31)$$

**3.2. Spin in Many-Electron Systems.** For a wave function which describes multiple particles, there are analogous spin operators  $\hat{\mathcal{S}}_i$  which are defined as

$$\hat{\mathcal{S}}_z = \sum_j^N \hat{S}_z(j) \quad (32)$$

and equivalently for the other 2 spin operators. Hence, it is just a sum of 1-electron operators! In the specific case of  $\hat{\mathcal{S}}_z$ , for some  $N$  spin 1/2 particles, it is fairly simple to see that each term in the summation either contributes  $\pm \frac{\hbar}{2}$ . Hence, the total  $m_z$  value is given as the difference between spin up and spin down particles multiplied by  $\frac{\hbar}{2}$ .

The total  $\hat{\mathcal{S}}^2$  operator is much more complicated since it is not simply a sum of 1-electron operators!

$$\hat{\mathcal{S}}^2 \neq \sum_j^N \hat{S}^2(j) \quad (33)$$

Instead, we can use similar relations as in the single particle case to write that

$$\begin{aligned} \hat{\mathcal{S}}^2 &= \hat{\mathcal{S}}_+ \hat{\mathcal{S}}_- - \hat{\mathcal{S}}_z + \hat{\mathcal{S}}_z^2 \\ &= \hat{\mathcal{S}}_- \hat{\mathcal{S}}_+ + \hat{\mathcal{S}}_z + \hat{\mathcal{S}}_z^2 \end{aligned} \quad (34)$$

As an example, let's consider 2 spin 1/2 particles. We know that all possible states in are given by

$$|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle \quad (35)$$

And we can label them as eigenstates of  $\hat{S}_z(i)$  and  $\hat{S}^2(i)$ . However, it is much more convenient to work in the basis of eigenstates of  $\hat{\mathcal{S}}_z$  and  $\hat{\mathcal{S}}^2$ . Now, it is clear that  $|\uparrow\uparrow\rangle$  has a  $m$  of 1 since it is the sum of  $m_1 + m_2$ . We can further identify then that it does not belong so a half-integer spin irrep, but must belong to either spin 1, spin 2, or higher. It is impossible for us to get a total spin of more than 1 since  $1/2 + 1/2 = 1$ , hence, this belongs to the spin 1 irrep. In particular, it is also a state of total spin  $s = 1$ ! So that, we could label

$$|\uparrow\uparrow\rangle = |1, 1\rangle \quad (36)$$

Similarly, we can identify

$$|\downarrow\downarrow\rangle = |1, -1\rangle \quad (37)$$

And finally, we can find the third state in the singlet irrep by applying  $\hat{\mathcal{S}}_-$  to  $|\uparrow\uparrow\rangle$ .

$$\hat{\mathcal{S}}_- = \hat{S}_-(1) + \hat{S}_-(2) \quad (38)$$

$$\hat{\mathcal{S}}_-|1, 1\rangle = (\hat{S}_-(1) + \hat{S}_-(2))|\uparrow\uparrow\rangle$$

$$\sqrt{2}|1, 0\rangle = \sqrt{1}|\downarrow\uparrow\rangle + \sqrt{1}|\uparrow\downarrow\rangle \quad (39)$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle + |\uparrow\downarrow\rangle)$$

For the last state, we need to find the state orthogonal to these 3 states, and we can find this by noting that

$$|0, 0\rangle = \frac{1}{\sqrt{2}}(|\downarrow\uparrow\rangle - |\uparrow\downarrow\rangle) \quad (40)$$

This gives us the basis for the 2 spin-1/2 particles which are eigenstates of total spin  $\hat{\mathcal{S}}^2$  and  $\hat{\mathcal{S}}_z$ . Note, the algebra works out such that we started with  $(S_1 = 1/2) \otimes (S_2 = 1/2)$ , a 4-dimension space. However, we moved to the  $(S = 1) \oplus (S = 0)$  (also 4-dimensional) vector space representation. In general, one can always go from the single particle spin/angular momentum basis to the total wave function spin/angular momentum basis using the Clebsh-Gordon coefficients. It is not particularly instructive to list these out, or their recursion relations, but it is important to know that they exist and they tell us how to go between these two representations.

**3.3. Addition of Angular Momenta.** What we have just seen in the prior section is an example of addition of angular momenta (recall that spin is just an intrinsic angular momentum). Lets try to generalize this a bit. Lets suppose that we have 2  $\hat{J}$  operators (they can be  $\hat{L}$  or  $\hat{S}$ , but for the context of this course, we can take them to be 2 spin operators for 2 particles), labeled  $\hat{J}_1$  and  $\hat{J}_2$ . Now, each operator satisfies the angular momenta algebra and, from before commutes with each other

$$[\hat{J}_1, \hat{J}_2] = 0 \quad (41)$$

The total angular momenta (or spin) for the system is given by  $\hat{J} = \hat{J}_1 + \hat{J}_2$ , and this also satisfies the correct angular momenta algebra

$$[\hat{J}_i, \hat{J}_j] = i\hbar\epsilon_{ijk}\hat{J}_k \quad (42)$$

Now, because of the commutation relations, we can form a basis either with

$$\hat{J}_1^2, \hat{J}_2^2, \hat{J}_{1z}, \hat{J}_{2z} \quad (43)$$

or

$$\hat{j}^2, \hat{J}_z, \hat{J}_1^2, \hat{J}_2^2 \quad (44)$$

In the former case, we can label the states using  $j_1, j_2, m_1, m_2$  such that

$$\hat{J}_i^2 |j_1, j_2, m_1, m_2\rangle = \hbar^2 j_i(j_i + 1) |j_1, j_2, m_1, m_2\rangle \quad (45)$$

$$\hat{J}_{iz} |j_1, j_2, m_1, m_2\rangle = \hbar m_i |j_1, j_2, m_1, m_2\rangle \quad (46)$$

For the latter basis, we have to first observe that  $[\hat{j}^2, \hat{J}_i^2] = 0$ . We can write  $\hat{j}^2$  as

$$\hat{j}^2 = \hat{J}_1^2 + \hat{J}_2^2 + 2\hat{J}_{1z}\hat{J}_{2z} + \hat{J}_{1+}\hat{J}_{2-} + \hat{J}_{1-}\hat{J}_{2+} \quad (47)$$

Since each term commutes with  $\hat{J}_i^2$ , then it must commute with  $\hat{j}^2$ . So our alternative basis can be labeled by  $j, m, j_1, j_2$  with

$$\hat{J}_i^2 |j, m, j_1, j_2\rangle = \hbar^2 j_i(j_i + 1) |j, m, j_1, j_2\rangle \quad (48)$$

$$\hat{j}^2 |j, m, j_1, j_2\rangle = \hbar^2 j(j + 1) |j, m, j_1, j_2\rangle \quad (49)$$

There must exist a unitary matrix which relates these 2 basis!

$$|j, m, j_1, j_2\rangle = \sum_{m_1 m_2} |j_1, j_2, m_1, m_2\rangle \langle j_1, j_2, m_1, m_2 | j, m, j_1, j_2\rangle \quad (50)$$

In the summation we have what are called the Clebsch-Gordan coefficients:

$$\langle j_1, j_2, m_1, m_2 | j, m, j_1, j_2\rangle \quad (51)$$

Lets now discuss some properties:

- (1) They vanish if  $m \neq m_1 + m_2$
- (2) They vanish unless  $|j_1 - j_2| \leq j \leq j_1 + j_2$

Ah! This tells us which spin states can be formed by combining particles of different spin! If we revisit our trusty 2 spin-1/2 particles, we see that  $j_1 + j_2 = 1$  and  $|j_1 - j_2| = 0$ . So,  $j = 0, 1$  as we determined! The first condition on  $m$  makes sense, essentially the  $m$  value can be taken as the sum of the individual spin components.

I will briefly mention that there also exists recursion relations for the Clebsch-Gordan coefficients, and ways to actually compute them, but they are not particularly interesting and can be found elsewhere. In fact, there is probably a website which can compute them for you!

**Example 3** (Spin 1 and Spin 1/2 Particle). Suppose we had 2 particles, one of spin 1 and the other of spin  $\frac{1}{2}$ . We want to know write our Hilbert space in terms of the irreducible representations of the total spin operator. That is, determine what are the possible basis stats ( $|j, m\rangle$ ). We know that the underlying Hilbert space is given as

$$1 \otimes \frac{1}{2} \quad (52)$$

which has a total dimension of  $3 \times 2 = 6$ . Now, from the Clebsch-Gordan coefficient properties, we know that  $|j_1 - j_2| \leq j \leq j_1 + j_2$  and hence

$$\frac{1}{2} \leq j \leq \frac{3}{2} \quad (53)$$

So,  $j$  can be either  $\frac{1}{2}, 1$ , or  $\frac{3}{2}$ . We know that  $\frac{3}{2}$  is possible since from the  $m$  values,  $1 + 1/2 = 3/2$ . And this subspace is of dimension 4. So the other subspace needs to have a dimension



of less than 2. Ah, this excludes the spin 1 subspace which has dimension 3, and leaves us instead with spin  $\frac{1}{2}$  subspace. So we can say that (pictorially)

$$1 \otimes \frac{1}{2} \cong \frac{3}{2} \oplus \frac{1}{2} \quad (54)$$

And indeed the dimensionality works out. This means that for a system with a spin 1 particle and a spin  $\frac{1}{2}$  particle, the allowed total spin is  $\frac{3}{2}$  and  $\frac{1}{2}$ , with the normal degeneracy (4 for  $\frac{3}{2}$  and 2 for  $\frac{1}{2}$ ).

We will see later that since the electronic Hamiltonian (neglecting relativistic effects/spin-orbit coupling) commutes with the total spin operator, so our final eigenstates can be represented in terms of  $|j, m\rangle$ . Thus, our trial wave functions should already be expressed in the basis of  $j, m$  quantum numbers rather than the single particle  $m_1, m_2$  basis so that our final variational solutions has the correct spin symmetry! Recall that the variational condition does not enforce symmetries that are not present in your trial wave function, and so we must embed them *a priori*.

#### REFERENCES

- [1] David Feller. The role of databases in support of computational chemistry calculations. *J. Comput. Chem.*, 17:1571–1586, 1996.
- [2] W. J. Hehre, R. F. Stewart, and J. A. Pople. Self-consistent molecular-orbital methods. i. use of gaussian expansions of slater-type atomic orbitals. *J. Chem. Phys.*, 51:2657–2664, 1969.
- [3] Benjamin P. Pritchard, Doaa Altarawy, Brett Didier, Tara D. Gibsom, and Theresa L. Windus. A new basis set exchange: An open, up-to-date resource for the molecular sciences community. *J. Chem. Inf. Model.*, 59:4814–4820, 2019.
- [4] Karen L. Schuchardt, Brett T. Didier, Todd Elsethagen, Lisong Sun, Vidhya Gurumoorthi, Jared Chase, Jun Li, and Theresa L. Windus. Basis set exchange: A community database for computational sciences. *J. Chem. Inf. Model.*, 47:1045–1052, 2007.