Advanced Quantum Mechanics

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Lecture #13

Quantum Mechanics of Many Particles

Recap of Last Class

QM of many identical particles: problem with tensor product states

2 particle states: permutation symmetry, Bosons and Fermions

3 particle states

N particle (anti) symmetrized states

(Anti) symmetrization of wavefunctions: Permanents and Determinants

Multi Electron Atoms: Case of Carbon

Multi-Electron Atoms

$$H = \sum_i \frac{p_i^2}{2m} - Ze^2 \sum_i \frac{1}{r_i} + \sum_i U(r_i) + \xi \sum_i \vec{L}_i \cdot \vec{S}_i + \sum_{ij}{}' \frac{e^2}{|r_i - r_j|} - \sum_{ij} U(r_i)\delta_{ij}$$

Start with screened Coulomb potential : degeneracy of l levels are lifted

(n,l) levels are filled according to Pauli exclusion principle starting from lowest one

Stable electronic shells corresponding to filled orbitals.

What happens to atoms which have partially filled levels?

Think about electrons in the partially filled level only

Consider Carbon atom: 6 electrons

$1s^2\ 2s^2\ 2p^2$

n= 1, l=0 level will have 2 e with spin ↑ and ↓

n= 2, l=0 level will have 2 e with spin ↑ and ↓

n= 2, l=1 level will have 2 e

Which l orbitals would be occupied and what is the spin config of the 2p electrons?

Each electron can occupy 3 X 2 =6 states, so there are 36 states in all

The Case of Carbon

The wavefunction of two non-interacting atoms occupying state m and n (given by both L_z and S_z)

$$\psi_F(x_1, x_2) = \begin{pmatrix} \phi_m(x_1) & \phi_m(x_2) \\ \phi_n(x_1) & \phi_n(x_2) \end{pmatrix}$$

The Slater determinant implies that there are actually 15 states consistent with Fermi statistics

You simply choose 2 out of the 6 states, making sure that they are different.

What are the quantum numbers of these 15 states?

If SO coupling is neglected, spin and orbital part can be treated separately

$$\psi_F(x_1, x_2) = \chi(s_1, s_2)\phi(x_1, x_2)$$

Spin states of 2 spin 1/2 particles : $S = S_1 + S_2$

Triplet States

$$|1/2, 1/2\rangle \quad \frac{1}{\sqrt{2}}(|1/2, -1/2\rangle + |-1/2, 1/2\rangle) \quad |-1/2, -1/2\rangle$$

Symmetric under exchange

Singlet States

$$\frac{1}{\sqrt{2}}(|1/2, -1/2\rangle - |-1/2, 1/2\rangle)$$

Anti-symmetric under exchange

The Case of Carbon

Orbital states of 2 l=1 particles $L=L_1+L_2$ (Eigenstates of total angular momentum)

L=2, 1, 0 states Consider $L=L_1+L_2$, where L_1 and L_2 transform according to the l irrep

States with L=2l are symmetric under exchange of 2 particles

$|2l, 2l\rangle = |l\rangle|l\rangle$ is symmetric under $1 \rightleftarrows 2$

|j,m> |m_1,m_2>

|j= 2l, m> is obtained from |j=2l,m=2l> by acting with $L^- = L_1^- + L_2^-$

Since L^- is symmetric under $1 \rightleftarrows 2$, |j= 2l, m> is symmetric under $1 \rightleftarrows 2$

States with L=2l-1 are anti symmetric under exchange of 2 particles

$$|2l-1, 2l-1\rangle = a|l-1\rangle|l\rangle + b|l\rangle|l-1\rangle$$

$$= [ac_l L_1^{-1} + bc_l L_2^-]|l\rangle|l\rangle \quad = c_l \left[\frac{a+b}{2}(L_1^{-1} + L_2^-) + \frac{a-b}{2}(L_1^{-1} - L_2^-)\right]|l\rangle|l\rangle$$

$$= c_l \frac{(a+b)}{2}|2l, 2l-1\rangle + c_l \frac{(a-b)}{2}(L_1^{-1} - L_2^-)|l\rangle|l\rangle$$

Since <2l,2l-1| 2l-1,2l-1> =0, a= -b ⟶ $|2l-1, 2l-1\rangle = ac_l(L_1^{-1} - L_2^-)|l\rangle|l\rangle$

|j= 2l-1, m> is obtained from |j=2l-1,m=2l-1> by acting with $L^- = L_1^- + L_2^-$ ⟶ Antisymmetric

The Case of Carbon

Similarly |2l-2,2l-2> can be written in terms of |l,l> and same orthogonality arguments show it to be symmetric under $1 \rightleftarrows 2$

Thus 2l, 2l-2, 2l-4 etc are symmetric under exchange, while 2l-1, 2l-3 etc are antisymmetric

For half-integer valued l, 2l is odd, so odd irreps are symmetric while even irreps are antisymmetric

S=1 is symmetric, S=0 is antisymmetric

For integer valued l, 2l is even, so even irreps are symmetric while odd irreps are antisymmetric

L=2,0 is symmetric, L=1 is antisymmetric

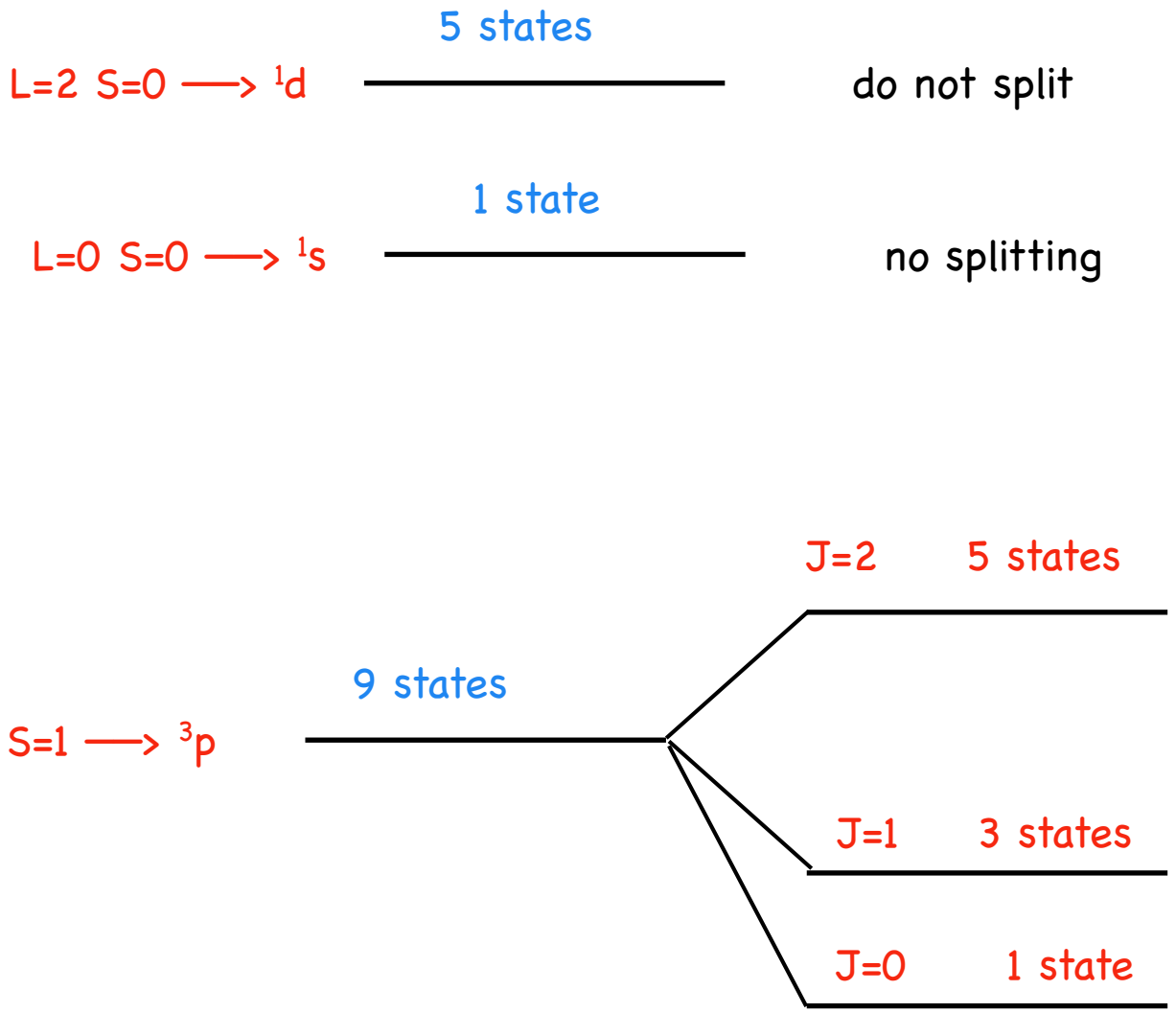
Since the wavefn (orbital + spin part) needs to be antisymmetric, possible combinations are

L=0 S=0 ⟶ ^{1}s L=2 S=0 ⟶ ^{1}d L=1 S=1 ⟶ ^{3}p $^{2S+1}$L Spectroscopic terms

9 states	1 state	5 states
L=1 S=1 ⟶ ^{3}p	L=0 S=0 ⟶ ^{1}s	L=2 S=0 ⟶ ^{1}d

The Case of Carbon: Spin Orbit Coupling

Splitting of the terms



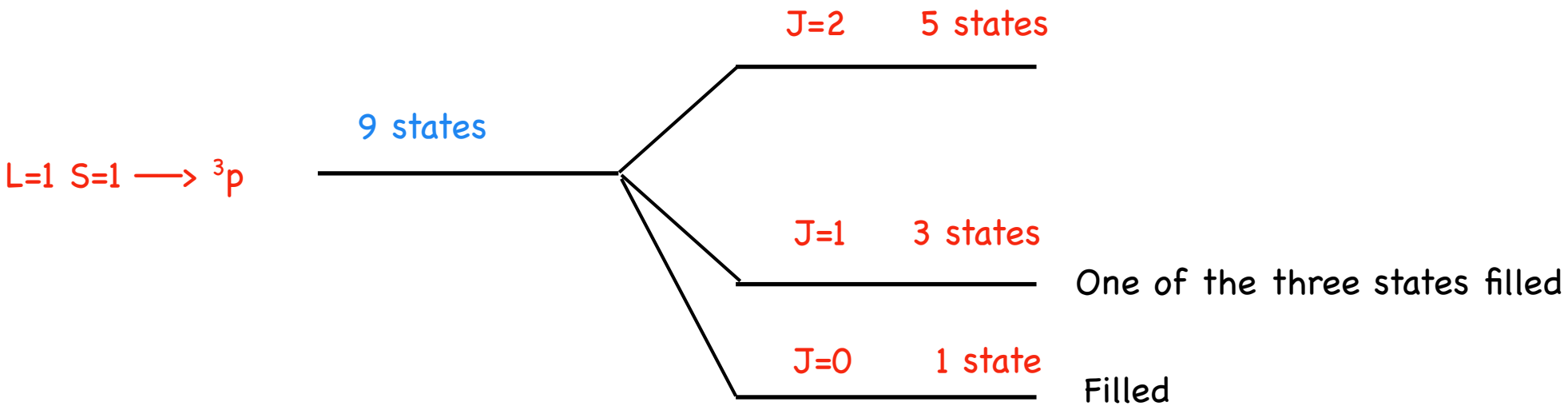
The Case of Carbon: Hund's Rule

Hund's Rule: State with largest multiplicity (largest spin) makes atoms more stable (lower energy)

In Antisymmetric orbital wavefunctions, the probability of two electrons occupying same pos. is 0

Electrons interact with repulsive Coulomb repulsion ~ 1/r. They can minimize this energy by staying as far apart, subject to other constraints (read other contribution to energy). So, anti-symmetric orbital wavefunctions and hence symmetric spin wfn.s are preferred. For 2 electrons S=1, L=1 would be preferred from Hund's coupling

Effective active degree of freedom : L=1,S=1 object



The Case of Nitrogen: 3 valence Electron

One can extend similar analysis to 3 valence electrons (N has 7 electrons $1s^2\ 2s^2\ 2p^3$)

The permutation symmetry group is S_3

	{E}	{R	{R
T	1	1	1
T	1	1	-1
T	2	-1	0

S_3 is non-Abelian and has a 2d irrep

Note that the full wfn (spin + orbital part) should transform according to $T^{(a)}$, but the orbital and the spin parts can individually transform according to any irrep including $T^{(m)}$ which is a mixed irrep (neither symmetric nor antisymmetric)

$T^{(a)}$ occurs in the reduction of $T^{(a)} \times T^{(s)}$

$T^{(s)} \times T^{(a)}$

$T^{(m)} \times T^{(m)}$

So, any of these are possibilities

Note, in the last case the two irreps correspond to orbital and spin states, so no symmetrization is required

Details to be worked out in HW

Occupation Numbers

Normalized Basis States in $\mathcal{B}_N$ and $\mathcal{F}_N$:

$$|\alpha_1, ...\alpha_N) = \frac{1}{\sqrt{\prod_\alpha n_\alpha!}} |\alpha_1, ...\alpha_N\} = \frac{1}{\sqrt{N! \prod_\alpha n_\alpha!}} \sum_{P_N} (\zeta)^{P_N} P_N[|\alpha_1, ...\alpha_N\rangle]$$

- The ordering 1,2,..N is irrelevant, as we are summing over all permutations anyway.
- States can be identified by how many times different single-particle states $|\alpha>$ occur in the string $|\alpha_1,... \alpha_N)$.
- Equivalent info: Specifying the occupation n_α of all the states $\{|\alpha>\}$ which form the basis in the single particle Hilbert space.

For a N particle state, $\sum_\alpha n_\alpha = N$. For Fermions, n

- Implicit assumption of a particular SP basis; e.g. momentum, position, S.H.O. states etc.
- Formalism independent of choice of basis. The details will vary.
- For a N particle state, specify infinite no. of occupation numbers. Instead of just a n-bit string, we have added a lot of redundancy to our description.

Same states represented by different info. (Anti) symmetrization is implicit

Occupation Numbers and Fock Space

Relax the condition $\sum_\alpha n_\alpha = N$

A Hilbert space where total no. of particles can vary. Direct sum of the (anti)symmetrized Hilbert space of Bosons(Fermions) for different total particle numbers N

$$\mathcal{B} = \oplus_N \mathcal{B}_N \qquad\qquad \mathcal{F} = \oplus_N \mathcal{F}_N$$

This space is called a Fock Space. States $|n_1, n_2, ...\rangle$ form a complete basis in this space, where 1,2,.. is SP basis states, rather than the particle number.

$$|\psi\rangle = \alpha|\psi_1\rangle + \beta|\psi_2\rangle + \gamma|\psi_3\rangle + ...$$

State with 1 part. State with 2 part. State with 3 part.

No. of particles is not conserved

- Work in this space and project onto the fixed total number subspace at the end.

Projecting onto fixed total No. subspace is easier than projecting into the (anti)symmetric sector.

- For systems with very large N, varying the number from N to N+1 should not make much difference in thermodynamic properties we wish to calculate.

OK if the distribution of the total number of particles is narrowly concentrated around the avg.

Creation and Annihilation Operators

Consider a SP basis labeled by λ. The creation operator for SP state λ is defined by

$$a^\dagger_\lambda|\lambda_1,...\lambda_N) = \sqrt{n_\lambda+1}|\lambda,\lambda_1,...\lambda_N) \qquad a^\dagger_\lambda|n_1,..n_\lambda,..\rangle = \sqrt{n_\lambda+1}|n_1,..n_\lambda+1,...\rangle$$

- By construction, the creation operator takes a (anti)symmetrized state to another (anti)symmetrized state. Keeps states within the Fock space.
- The creation operator takes a state in $\mathcal{B}_N$ ($\mathcal{F}_N$) to a state in $\mathcal{B}_{N+1}$ ($\mathcal{F}_{N+1}$). So it acts in $\mathcal{B}$ ($\mathcal{F}$)

Similarly, the annihilation operator for the state λ is defined by

for Bosons

$$a_\lambda|\lambda,\lambda_1,...\lambda_N) = \sqrt{n_\lambda}|\lambda_1,...\lambda_N)$$

for Fermions

$$a_{\lambda_i}|\lambda,\lambda_1,..\lambda_i,..\lambda_N) = (-1)^{i-1}|\lambda_1,...\lambda_N)$$

= 0 if λ_i is unoccupied

- By construction, the annihilation operator takes a (anti)symmetrized state to another (anti)symmetrized state. Keeps states within the Fock space.
- The annihilation operator takes a state in $\mathcal{B}_N$ ($\mathcal{F}_N$) to a state in $\mathcal{B}_{N-1}$ ($\mathcal{F}_{N-1}$). So it acts in $\mathcal{B}$ ($\mathcal{F}$)

Creation and Annihilation Operators

$$a^\dagger_\lambda a^\dagger_\mu |\lambda_1, \lambda_2, ..\lambda_N\} = |\lambda, \mu, \lambda_1, \lambda_2, ..\lambda_N\} = \zeta |\mu, \lambda, \lambda_1, \lambda_2, ..\lambda_N\} = \zeta a^\dagger_\mu a^\dagger_\lambda |\lambda_1, \lambda_2, ..\lambda_N\}$$

$$[a^\dagger_\lambda, a^\dagger_\mu]_\zeta = a^\dagger_\lambda a^\dagger_\mu - \zeta a^\dagger_\mu a^\dagger_\lambda = 0$$

For Bosons we have commutators, while
for Fermions we have anti-commutators

Note that for fermions the anti-commutation relation automatically gives $(a^\dagger_\lambda)^2 = 0$

Similarly we have $[a_\lambda, a_\mu]_\zeta = a_\lambda a_\mu - \zeta a_\mu a_\lambda = 0$

For Fermions: $(a_\lambda)^2 = 0$

$$a_\lambda a^\dagger_\mu |\lambda_1, \lambda_2, ..\lambda_N\} = a_\lambda |\mu, \lambda_1, \lambda_2, ..\lambda_N\} = \delta_{\lambda\mu} |\lambda_1, \lambda_2, ..\lambda_N\} + \textstyle\sum_{i=1}^{N} (\zeta)^i |\mu, \lambda_1, \lambda_2, .\bar{\lambda_i}..\lambda_N\}$$

$$= [\delta_{\lambda,\mu} + \zeta a^\dagger_\mu a_\lambda] |\lambda_1, \lambda_2, ..\lambda_N\}$$

$$[a_\lambda, a^\dagger_\mu]_\zeta = \delta_{\lambda,\mu}$$

We have hidden the (anti) symmetrization requirements in the (anti) commutation relations.

Can we write the many body QM in terms of these operators?

Occupation No. States with Creation/ Annihilation Operators

If we keep applying annihilation operator on any many-body state, we can make the occ. no. of any SP state 0. Thus, we are led to the vacuum state, which has no particles in any state.

$$a_\lambda|0\rangle = 0 \qquad \text{for all } \lambda$$

| 0> is a valid state in the Fock space and not the 0 on RHS of eqn.

Single Particle States: $|\lambda\rangle = a_\lambda^\dagger|0\rangle$ Two Particle States: $|\lambda_1, \lambda_2\} = a_{\lambda_1}^\dagger a_{\lambda_2}^\dagger|0\rangle$

Many Particle States: $$|n_{\lambda_1}, n_{\lambda_2}, ...\rangle = \prod_j \frac{\left(a_{\lambda_j}^\dagger\right)^{n_{\lambda_j}}}{\sqrt{n_{\lambda_j}!}}|0\rangle$$

Examples

Bosons:

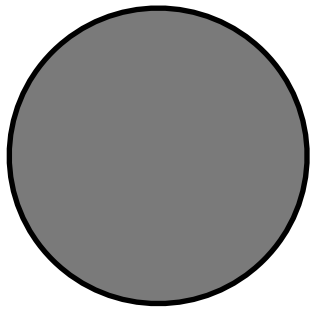
Ground State of N non-interacting free Bosons $$|\psi_0\rangle = \frac{\left(a_0^\dagger\right)^N}{\sqrt{N!}}|0\rangle$$

Macroscopic occupation of k=0 state

BEC

Fermions:

Ground State of N non-interacting free Fermions $|\psi\rangle = \prod_{\sigma,|k|<k_F} c_{k\sigma}^\dagger|0\rangle$



Filled Fermi Sea

$$k_F^3 = 3\pi^2\frac{N}{V}$$

Many-Body Operators (1st Quantized form)

We need to define sensible operators which do not violate the indistinguishability of the particles

Examples of non-observables: Position of 3rd particle, K.E. of first 10 particles etc

Better Classification: 1-particle, 2-particle, 3-particle,.... N-particle operators.

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1 Particle Operators: Sum of N operators, each of which act on single-particle Hilbert space.

Kinetic energy: $\hat{T} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m}$ External Potential energy: $\hat{U} = \sum_{i=1}^{N} u(\hat{r}_i)$

For Tensor product states in $\mathcal{H}_N$ $\langle \beta_1, ...\beta_N | \mathcal{O}^1 | \alpha_1, ...\alpha_N \rangle = \sum_i \prod_{i \neq k} \langle \beta_k | \alpha_k \rangle \langle \beta_i | \mathcal{O}_i^1 | \alpha_i \rangle$

Many-Body Operators (1st Quantized form)

2 Particle Operators: Sum of N(N-1)/2 operators, one for each distinct pair of particles, each of which act on the two-particle Hilbert space.

Pairwise interaction between particles: $\hat{V} = \sum_{1 \le i < j \le N} v(\hat{r}_i, \hat{r}_j) \quad = \frac{1}{2} \sum_{i \neq j} v(\hat{r}_i, \hat{r}_j)$

For Tensor product states in $\mathcal{H}_N$ $\quad \langle \beta_1, ... \beta_N | \mathcal{O}^2 | \alpha_1, ... \alpha_N \rangle = \frac{1}{2} \sum_{i \neq j} \prod_{k \neq i,j} \langle \beta_k | \alpha_k \rangle \langle \beta_i, \beta_j | \mathcal{O}^2_{ij} | \alpha_i, \alpha_j \rangle$

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n-Particle Operators: Sum of operators, one for each distinct n-tuple of particles, each of which act on the n-particle Hilbert space.

n-body interactions $\quad V_n = \frac{1}{n!} \sum_{i_1 \neq i_2 \neq .. \neq i_n} v_n(\hat{r}_{i_1}, \hat{r}_{i_2}, .. \hat{r}_{i_n})$

For Tensor product states in $\mathcal{H}_N$

$$\langle \beta_1, ... \beta_N | \mathcal{O}^n | \alpha_1, ... \alpha_N \rangle = \frac{1}{n!} \sum_{i_1 \neq i_2 \neq .. \neq i_n} \prod_{k \neq i_1, i_2, .. i_n} \langle \beta_k | \alpha_k \rangle \langle \beta_{i_1}, \beta_{i_2}, .. \beta_{i_n} | \mathcal{O}^n_{i_1, i_2, .. i_n} | \alpha_{i_1}, \alpha_{i_2}, .. \alpha_{i_n} \rangle$$

Can we write these operators in terms of creation/annihilation operators?

Operators in 2nd Quantized Notation

1 particle operators $\hat{A} = \sum_i \hat{A}_i$

Generic 1-particle operator: $\hat{A}_i = \sum_{\alpha\beta} A_{\alpha\beta} |\alpha\rangle_i \, {}_i\langle\beta|$

where α and β are single particle states.

Let $\hat{A}_i = |\alpha\rangle_i \, {}_i\langle\beta|$

$$\hat{A}|\beta_1, ...\beta_i, ...\beta_N\} = \sum_i |\beta_1, ...\alpha_i ....\beta_N\} = a^\dagger_\alpha a_\beta |\beta_1, ...\beta_i, ...\beta_N\}$$

So, for the generic case $\boxed{\hat{A} = \sum_{\alpha\beta} A_{\alpha\beta} a^\dagger_\alpha a_\beta}$

Some Important examples:

Identity Operator $A_{\alpha\beta} = \delta_{\alpha\beta} \longrightarrow \hat{N} = \sum_\alpha a^\dagger_\alpha a_\alpha$ Total Number Operator

Real Space Density $\delta(x - x_i)\delta(x_i - x'_i) \longrightarrow \hat{\rho}(x) = a^\dagger_x a_x$

Kinetic Energy: $\sum_p \frac{p^2}{2m} a^\dagger_p a_p$

External Potential: $\sum_x U(x) a^\dagger_x a_x = \sum_x U(x) \hat{\rho}(x)$