1 Coulomb interaction Hamiltonian in the second-quantized form

General expressions for an arbitrary orbital moment

Hamiltonian of a multiorbital electron system in the second-quantization representation:

$$\hat{H} = \sum_{\langle\alpha\beta\rangle\sigma} h_{ij} c^\dagger_{\alpha\sigma} c_{\beta\sigma} + \frac{1}{2} \sum_{\substack{\alpha\beta\gamma\delta \\ \sigma\sigma'}} U^{\sigma\sigma'}_{\alpha\beta\gamma\delta} c^\dagger_{\alpha\sigma} c^\dagger_{\beta\sigma'} c_{\gamma\sigma'} c_{\delta\sigma} \tag{1}$$

In the simplest case orbital indices $\alpha, \beta, \gamma, \delta$ in the quartic part of the Hamiltonian correspond to electrons localized on a single atom and occupying the same subshell with orbital moment l (the one-electron states are distinguished by their moment projection):

$$\hat{H}_{int} = \frac{1}{2} \sum_{\substack{m'_1 m'_2 m_1 m_2 \\ \sigma\sigma'}} U^{\sigma\sigma'}_{m'_1 m'_2 m_1 m_2} c^\dagger_{m'_1\sigma} c^\dagger_{m'_2\sigma'} c_{m_1\sigma'} c_{m_2\sigma} \tag{2}$$

Components of tensor $U^{\sigma\sigma'}_{m'_1 m'_2 m_1 m_2}$ are determined by matrix elements of the Coulomb interaction operator, calculated with two-particle wave functions.

$$U^{\sigma\sigma'}_{m'_1 m'_2 m_1 m_2} = \left\langle \sigma l m'_1; \sigma' l m'_2 \left| \frac{e^2}{|\hat{\mathbf{r}} - \hat{\mathbf{r}}'|} \right| \sigma l m_2; \sigma' l m_1 \right\rangle \tag{3}$$

One-particle atomic wave function of an electron:

$$\psi_{\sigma l m}(\mathbf{r}, s) = \chi_\sigma(s) \varphi_l(r) Y_{lm}(\Omega), \quad \Omega = (\theta, \phi), \quad d\Omega = \sin\theta d\theta d\phi \tag{4}$$

There is a well-known expansion of the Coulomb potential which is convenient for calculating the matrix elements:

$$\frac{e^2}{|\mathbf{r} - \mathbf{r}'|} = e^2 \sum_{k=0}^{\infty} \frac{4\pi}{2k+1} \frac{r^k_<}{r^{k+1}_>} \sum_{q=-k}^{k} Y^*_{kq}(\Omega) Y_{kq}(\Omega'), \quad r_> = \max\{|\mathbf{r}|, |\mathbf{r}'|\}, \ r_< = \min\{|\mathbf{r}|, |\mathbf{r}'|\} \tag{5}$$

An explicit form of the matrix element reads:

$$\left\langle \sigma l m'_1; \sigma' l m'_2 \left| \frac{e^2}{|\hat{\mathbf{r}} - \hat{\mathbf{r}}'|} \right| \sigma l m_2; \sigma' l m_1 \right\rangle =$$

$$= \sum_{ss'} \int d^3\mathbf{r}\ d^3\mathbf{r}' (\psi_{\sigma l m'_1}(\mathbf{r}, s) \psi_{\sigma' l m'_2}(\mathbf{r}', s'))^* \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} (\psi_{\sigma l m_2}(\mathbf{r}, s) \psi_{\sigma' l m_1}(\mathbf{r}', s')) =$$

$$= \sum_{k=0}^{\infty} \underbrace{e^2 \iint_0^{+\infty} r^2 dr\ r'^2 dr' |\varphi_l(r)|^2 |\varphi_l(r')|^2 \frac{r^k_<}{r^{k+1}_>}}_{\equiv F^k} A_k(m'_1, m'_2, m_2, m_1) = \sum_{k=0}^{\infty} F^k A_k(m'_1, m'_2, m_2, m_1) \tag{6}$$

F^k is the radial part of the matrix element. Its value depends on the choice of $\varphi_l(r)$, that is arbitrary to some extent. A_k is the angular part of the matrix element.

$$A_k(m'_1, m'_2, m_2, m_1) =$$
$$\frac{4\pi}{2k+1} \sum_{q=-k}^{k} \iint d\Omega\ d\Omega' Y^*_{lm'_1}(\Omega) Y^*_{lm'_2}(\Omega') Y^*_{kq}(\Omega) Y_{kq}(\Omega') Y_{lm_2}(\Omega) Y_{lm_1}(\Omega') \tag{7}$$

We can get rid of a complex conjugate in the last expression using an identity $Y^*_{lm}(\Omega) = (-1)^m Y_{l-m}(\Omega)$:

$$A_k(m'_1, m'_2, m_2, m_1) =$$
$$\frac{4\pi}{2k+1} \sum_{q=-k}^{k} (-1)^{m'_1+q+m'_2} \iint d\Omega\ d\Omega' Y_{l-m'_1}(\Omega) Y_{l-m'_2}(\Omega') Y_{k-q}(\Omega) Y_{kq}(\Omega') Y_{lm_2}(\Omega) Y_{lm_1}(\Omega') \tag{8}$$

To calculate the angular part of the matrix elements we make use of an addition theorem for spherical harmonics (addition of moments):

$$\int Y_{l_1 m_1}(\Omega) Y_{l_2 m_2}(\Omega) Y_{l_3 m_3}(\Omega)\, d\Omega = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \tag{9}$$

For A_k we eventually come to:

$$A_k(m_1', m_2', m_2, m_1) = (2l+1)^2 \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{q=-k}^{k} (-1)^{m_1'+q+m_2'} \begin{pmatrix} l & k & l \\ -m_1' & -q & m_2 \end{pmatrix} \begin{pmatrix} l & k & l \\ -m_2' & q & m_1 \end{pmatrix}$$

Let us calculate the nonzero angular matrix elements for particular values of l.

S-orbital - $l = 0$

$$A_0(0,0,0,0) = 1 \tag{10}$$

$$\hat{H}_{int} = U n_\uparrow n_\downarrow, \qquad U \equiv F^{\mathbf{0}} \tag{11}$$

P-orbital - $l = 1$

$$A_0(m_2, m_1, m_2, m_1) = 1 \tag{12}$$

$$A_2(m,0,m,0) = A_2(0,m,0,m) = -2/25 \ (m = \pm 1) \tag{13}$$

$$A_2(m,0,0,m) = A_2(0,m,m,0) = -A_2(0,0,m,-m) = -A_2(m,-m,0,0) = 3/25 \ (m = \pm 1) \tag{14}$$

$$A_2(m,-m,-m,m) = 6A_2(m,-m,m,-m) = 6/25 \ (m = \pm 1) \tag{15}$$

$$A_2(0,0,0,0) = 4A_2(-1,-1,-1,-1) = 4A_2(1,1,1,1) = 4/25 \tag{16}$$

$$\hat{H}_{int} = \frac{F^{\mathbf{0}} - F^{\mathbf{2}}/5}{2} \sum_{m \neq m', \sigma} n_{m\sigma} n_{m'\sigma} + \frac{F^{\mathbf{0}}}{2} \sum_{mm',\sigma} n_{m\sigma} n_{m'\bar{\sigma}} + \frac{1}{2}\frac{F^{\mathbf{2}}}{25} \sum_{mm',\sigma} W^{(1)}_{mm'} n_{m,\sigma} n_{m',\bar{\sigma}} +$$
$$+ \frac{1}{2}\frac{F^{\mathbf{2}}}{25} \sum_{mm',\sigma} W^{(2)}_{mm'} c^\dagger_{m\sigma} c^\dagger_{m'\bar{\sigma}} c_{m\bar{\sigma}} c_{m'\sigma} + \frac{1}{2}\frac{F^{\mathbf{2}}}{25} \sum_{mm',\sigma} W^{(3)}_{mm'} c^\dagger_{m\sigma} c^\dagger_{-m\bar{\sigma}} c_{m'\bar{\sigma}} c_{-m'\sigma}$$

$$W^{(1)} = \begin{pmatrix} 1 & -2 & 1 \\ -2 & 4 & -2 \\ 1 & -2 & 1 \end{pmatrix} \quad W^{(2)} = \begin{pmatrix} 0 & 3 & 6 \\ 3 & 0 & 3 \\ 6 & 3 & 0 \end{pmatrix} \quad W^{(3)} = \begin{pmatrix} 0 & -3 & 0 \\ -3 & 0 & -3 \\ 0 & -3 & 0 \end{pmatrix} \tag{17}$$

In the case of p-orbitals ($l = 1$) in addition to the basis of spherical harmonics $Y_{lm}(\Omega)$ the basis of cubic harmonics is of use to represent the angular part of a wave function.

$$Y_{1x}(\Omega) = \frac{1}{\sqrt{2}}(Y_{11}(\Omega) - Y_{1-1}(\Omega))$$
$$Y_{1y}(\Omega) = \frac{1}{i\sqrt{2}}(Y_{11}(\Omega) + Y_{1-1}(\Omega))$$
$$Y_{1z}(\Omega) = Y_{10}(\Omega)$$

These functions are eigenfunctions of operators $\hat{l}_x$, $\hat{l}_y$ and $\hat{l}_z$ corresponding to zero eigenvalues.

The interaction Hamiltonian in this basis can be easily obtained with help of formulae relating operators $c^\dagger_{m\sigma}$, $c_{m\sigma}$ with operators $c^\dagger_{p\sigma}$, $c_{p\sigma}$ $(p = x, y, z)$:

$$c^\dagger_{m\sigma} = \sum_p \langle Y_{1p}|Y_{1m}\rangle c^\dagger_{p\sigma}$$

$$c_{m\sigma} = \sum_p \langle Y_{1p}|Y_{1m}\rangle^* c_{p\sigma}$$

$$\hat{H}_{int} = \frac{U}{2}\sum_{p\sigma} n_{p\sigma}n_{p\bar{\sigma}} + \frac{U-2J}{2}\sum_{p\neq p',\sigma} n_{p\sigma}n_{p'\bar{\sigma}} + \frac{U-3J}{2}\sum_{p\neq p',\sigma} n_{p\sigma}n_{p'\sigma} - \\ -\frac{J}{2}\sum_{p\neq p',\sigma}(c^\dagger_{p\sigma}c^\dagger_{p'\bar{\sigma}}c_{p'\sigma}c_{p\bar{\sigma}} + c^\dagger_{p'\sigma}c^\dagger_{p'\bar{\sigma}}c_{p\sigma}c_{p\bar{\sigma}}) \tag{18}$$

$$U \equiv F^{\mathbf{0}} + \frac{4F^{\mathbf{2}}}{25}, \quad J \equiv \frac{3F^{\mathbf{2}}}{25} \tag{19}$$

This last expression can be rewritten in a slightly different form with terms $n_{p\sigma} - 1/2$ explicitly marked out.

$$\hat{H}_{int} = \mathrm{const} + 5\left(\frac{U}{2} - J\right)\sum_{p\sigma}\left(n_{p\sigma} - \frac{1}{2}\right) + \tag{20}$$

$$+\frac{U}{2}\sum_{p\sigma}\left(n_{p\sigma} - \frac{1}{2}\right)\left(n_{p\bar{\sigma}} - \frac{1}{2}\right) + \frac{U-2J}{2}\sum_{p\neq p',\sigma}\left(n_{p\sigma} - \frac{1}{2}\right)\left(n_{p'\bar{\sigma}} - \frac{1}{2}\right) + \frac{U-3J}{2}\sum_{p\neq p',\sigma}\left(n_{p\sigma} - \frac{1}{2}\right)\left(n_{p'\sigma} - \frac{1}{2}\right) - \\ -\frac{J}{2}\sum_{p\neq p',\sigma}(c^\dagger_{p\sigma}c^\dagger_{p'\bar{\sigma}}c_{p'\sigma}c_{p\bar{\sigma}} + c^\dagger_{p'\sigma}c^\dagger_{p'\bar{\sigma}}c_{p\sigma}c_{p\bar{\sigma}})$$

D-orbital - $l = 2$

$$\hat{H}_{int} = \frac{F^{\mathbf{0}}}{2} \sum_{mm',\sigma} n_{m\sigma} n_{m'\bar{\sigma}} + \frac{1}{2} \sum_{m \neq m',\sigma} (F^{\mathbf{0}} + \frac{F^{\mathbf{2}}}{49} W^{(0)}_{mm'} - \frac{F^{\mathbf{4}}}{147} Z^{(0)}_{mm'}) n_{m\sigma} n_{m'\sigma} +$$
$$+ \frac{1}{2} \sum_{mm',\sigma} (\frac{F^{\mathbf{2}}}{49} W^{(1)}_{mm'} + \frac{F^{\mathbf{4}}}{441} Z^{(1)}_{mm'}) n_{m,\sigma} n_{m',\bar{\sigma}} +$$
$$+ \sum_{m=\pm 1,\sigma} \frac{3}{49} (-F^{\mathbf{2}} + F^{\mathbf{4}}) (c^{\dagger}_{0\sigma} c^{\dagger}_{m\sigma} c_{-m\sigma} c_{2m\sigma} + c^{\dagger}_{m\sigma} c^{\dagger}_{0\sigma} c_{2m\sigma} c_{-m\sigma} + c^{\dagger}_{-m\sigma} c^{\dagger}_{2m\sigma} c_{0\sigma} c_{m\sigma} + c^{\dagger}_{2m\sigma} c^{\dagger}_{-m\sigma} c_{m\sigma} c_{0\sigma}) + \quad (21)$$
$$+ \frac{1}{2} \sum_{mm',\sigma} (\frac{F^{\mathbf{2}}}{49} W^{(2)}_{mm'} + \frac{5F^{\mathbf{4}}}{441} Z^{(2)}_{mm'}) c^{\dagger}_{m\sigma} c^{\dagger}_{m'\bar{\sigma}} c_{m\bar{\sigma}} c_{m'\sigma} + \frac{1}{2} \sum_{mm',\sigma} (\frac{F^{\mathbf{2}}}{49} W^{(3)}_{mm'} + \frac{5F^{\mathbf{4}}}{441} Z^{(3)}_{mm'}) c^{\dagger}_{m\sigma} c^{\dagger}_{-m\bar{\sigma}} c_{m'\bar{\sigma}} c_{-m'\sigma} +$$
$$+ \frac{\sqrt{6}}{49} (F^{\mathbf{2}} - \frac{5}{9} F^{\mathbf{4}}) \sum_{mm',\sigma} W^{(4)}_{mm'} (c^{\dagger}_{0\sigma} c^{\dagger}_{m\bar{\sigma}} c_{m'\bar{\sigma}} c_{m-m'\sigma} + c^{\dagger}_{m\sigma} c^{\dagger}_{0\bar{\sigma}} c_{m-m'\bar{\sigma}} c_{m'\sigma} + c^{\dagger}_{m'\sigma} c^{\dagger}_{m-m'\bar{\sigma}} c_{0\bar{\sigma}} c_{m\sigma} + c^{\dagger}_{m-m'\sigma} c^{\dagger}_{m'\bar{\sigma}} c_{m\bar{\sigma}} c_{0\sigma})$$

$$W^{(0)} = \begin{pmatrix} 0 & -8 & -8 & -4 & 4 \\ -8 & 0 & 1 & -5 & -2 \\ -8 & 1 & 0 & -8 & -8 \\ -2 & -5 & 1 & 0 & -8 \\ 4 & -4 & -8 & -8 & 0 \end{pmatrix} \quad Z^{(0)} = \begin{pmatrix} 0 & 3 & 3 & 13 & 23 \\ 3 & 0 & 18 & 8 & 13 \\ 3 & 18 & 0 & 18 & 3 \\ 13 & 8 & 18 & 0 & 3 \\ 23 & 13 & 3 & 3 & 0 \end{pmatrix} \tag{22}$$

$$W^{(1)} = \begin{pmatrix} 4 & -2 & -4 & -2 & 4 \\ -2 & 1 & 2 & 1 & -2 \\ -4 & 2 & 4 & 2 & -4 \\ -2 & 1 & 2 & 1 & -2 \\ 4 & -2 & -4 & -2 & 4 \end{pmatrix} \quad Z^{(1)} = \begin{pmatrix} 1 & -4 & 6 & -4 & 1 \\ -4 & 16 & -24 & 16 & -4 \\ 6 & -24 & 36 & -24 & 6 \\ -4 & 16 & -24 & 16 & -4 \\ 1 & -4 & 6 & -4 & 1 \end{pmatrix} \tag{23}$$

$$W^{(2)} = \begin{pmatrix} 0 & 6 & 4 & 0 & 0 \\ 6 & 0 & 1 & 6 & 0 \\ 4 & 1 & 0 & 1 & 4 \\ 0 & 6 & 1 & 0 & 6 \\ 0 & 0 & 4 & 6 & 0 \end{pmatrix} \quad Z^{(2)} = \begin{pmatrix} 0 & 1 & 3 & 7 & 14 \\ 1 & 0 & 6 & 8 & 7 \\ 3 & 6 & 0 & 6 & 3 \\ 7 & 8 & 6 & 0 & 1 \\ 14 & 7 & 3 & 1 & 0 \end{pmatrix} \tag{24}$$

$$W^{(3)} = \begin{pmatrix} 0 & -6 & 4 & 0 & 0 \\ -6 & 0 & -1 & 0 & 0 \\ 4 & -1 & 0 & -1 & 4 \\ 0 & 0 & -1 & 0 & -6 \\ 0 & 0 & 4 & -6 & 0 \end{pmatrix} \quad Z^{(3)} = \begin{pmatrix} 0 & -1 & 3 & -7 & 0 \\ -1 & 0 & -6 & 0 & -7 \\ 3 & -6 & 0 & -6 & 3 \\ -7 & 0 & -6 & 0 & -1 \\ 0 & -7 & 3 & -1 & 0 \end{pmatrix} \tag{25}$$

$$W^{(4)} = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 \\ 2 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 2 \\ 0 & 0 & 0 & 1 & 0 \end{pmatrix} \tag{26}$$

2 The Coulomb interaction Hamiltonian as a function of integrals of motion

2.1 S-orbital - $l = 0$

$$\hat{H}_{int} = U n_\uparrow n_\downarrow = \frac{U}{2}(n_\uparrow + n_\downarrow - 1)^2 + \frac{U}{2}(n_\uparrow + n_\downarrow - 1) = \frac{U}{2}(\hat{N} - 1)^2 + \frac{U}{2}(\hat{N} - 1) \tag{27}$$

The Hamiltonian with a chemical potential taken into account:

$$\hat{H} = -\mu\hat{N} + \hat{H}_{int} = -(\mu - \mu_0)(\hat{N} - 1) + \frac{U}{2}(\hat{N} - 1)^2 - \mu, \tag{28}$$

where $\mu_0 = U/2$ is the chemical potential corresponding to the half-filling.

Spectrum of the Hamiltonian:

N	E	Degree of degeneracy
0	0	1
1	$-\mu$	2
2	$-2\mu + U$	1

2.2 P-orbital - $l = 1$

Before switching to the second-quantization representation the interaction Hamiltonian had the following form:

$$\hat{H}_{int} = \frac{1}{2}\sum_{i \neq j} \hat{U}_{ij}, \quad \hat{U}_{ij} = \frac{e^2}{|\mathbf{r}_i - \mathbf{r}'_j|} \tag{29}$$

Let us find a representation of the pair coupling operator $\hat{U}_{ij}$ which is a linear combination of the simplest scalar operators $(\mathbf{s}_i \cdot \mathbf{s}_j)$ and $(\mathbf{l}_i \cdot \mathbf{l}_j)$:

$$\hat{U}_{ij} = \lambda_0 + \lambda_{ss}(\mathbf{s}_i \cdot \mathbf{s}_j) + \lambda_{ll}(\mathbf{l}_i \cdot \mathbf{l}_j) \tag{30}$$

Diagonalization of this operator is equivalent to a classification of states of two electrons with respect to their full spin and orbital moments (taking into account the antisymmetry). For the case under consideration (P-orbital) all two-electron states ($C_6^2 = 15$ in total) are split into 3 multiplets. If one state is taken from each multiplet and an average value of $\hat{U}_{ij}$ is calculated using this state, the result will be expressed through the matrix elements (3). This way we will get three independent equations to determine constants λ_0, λ_{ss} and λ_{ll}.

There are identities helpful in calculating the averages:

$$(\mathbf{s}_i \cdot \mathbf{s}_j) = \frac{1}{2}[(\mathbf{s}_i + \mathbf{s}_j)^2 - \mathbf{s}_i^2 - \mathbf{s}_j^2] = \frac{1}{2}\left[(\mathbf{s}_i + \mathbf{s}_j)^2 - \frac{3}{2}\right] \tag{31}$$

$$(\mathbf{l}_i \cdot \mathbf{l}_j) = \frac{1}{2}\left(l_+^i l_-^j + l_-^i l_+^j\right) + l_z^i l_z^j \tag{32}$$

Now we consider the 3 multiplets.

1. $(\mathbf{s}_i + \mathbf{s}_j)^2 = 0$, $(\mathbf{l}_i + \mathbf{l}_j)^2 = 0$ (s-singlet × l-singlet).

$$|\psi\rangle = \frac{1}{\sqrt{2}}[|\uparrow 0\rangle_i |\downarrow 0\rangle_j - |\downarrow 0\rangle_i |\uparrow 0\rangle_j]$$

$$(\mathbf{l}_i \cdot \mathbf{l}_j)|\psi\rangle = \frac{1}{\sqrt{2}}\frac{1}{2}[|\uparrow 1\rangle_i |\downarrow -1\rangle_j + |\uparrow -1\rangle_i |\downarrow 1\rangle_j - |\downarrow 1\rangle_i |\uparrow -1\rangle_j - |\downarrow -1\rangle_i |\uparrow 1\rangle_j]$$

$$\langle\psi|(\mathbf{l}_i \cdot \mathbf{l}_j)|\psi\rangle = 0, \quad \langle\psi|(\mathbf{s}_i \cdot \mathbf{s}_j)|\psi\rangle = -3/4$$

$$\langle\psi|\hat{U}_{ij}|\psi\rangle = \frac{1}{2}\left[\langle\uparrow 0;\downarrow 0|\hat{U}_{ij}|\uparrow 0;\downarrow 0\rangle + \langle\downarrow 0;\uparrow 0|\hat{U}_{ij}|\downarrow 0;\uparrow 0\rangle\right] =$$
$$= F^0 A_0(0,0,0,0) + F^2 A_2(0,0,0,0) = F^0 + (4/25)F^2$$

$$\lambda_0 + (-3/4)\lambda_{ss} = F^0 + (4/25)F^2 \tag{33}$$

2. $(\mathbf{s}_i + \mathbf{s}_j)^2 = 0$, $(\mathbf{l}_i + \mathbf{l}_j)^2 = 2(2+1)$ (s-singlet $\times$ l-pentaplet).

$$|\psi\rangle = \frac{1}{\sqrt{2}}[|\uparrow 1\rangle_i |\downarrow 1\rangle_j - |\downarrow 1\rangle_i |\uparrow 1\rangle_j]$$

$$(\mathbf{l}_i \cdot \mathbf{l}_j)|\psi\rangle = \frac{1}{\sqrt{2}}[|\uparrow 1\rangle_i |\downarrow 1\rangle_j - |\downarrow 1\rangle_i |\uparrow 1\rangle_j]$$

$$\langle\psi|(\mathbf{l}_i \cdot \mathbf{l}_j)|\psi\rangle = 1, \quad \langle\psi|(\mathbf{s}_i \cdot \mathbf{s}_j)|\psi\rangle = -3/4$$

$$\langle\psi|\hat{U}_{ij}|\psi\rangle = \frac{1}{2}\left[\langle\uparrow 1;\downarrow 1|\hat{U}_{ij}|\uparrow 1;\downarrow 1\rangle + \langle\downarrow 1;\uparrow 1|\hat{U}_{ij}|\downarrow 1;\uparrow 1\rangle\right] =$$
$$= F^0 A_0(1,1,1,1) + F^2 A_2(1,1,1,1) = F^0 + (1/25)F^2$$

$$\lambda_0 + (-3/4)\lambda_{ss} + \lambda_{ll} = F^0 + (1/25)F^2 \tag{34}$$

3. $(\mathbf{s}_i + \mathbf{s}_j)^2 = 1(1+1)$, $(\mathbf{l}_i + \mathbf{l}_j)^2 = 1(1+1)$ (s-triplet $\times$ l-triplet).

$$|\psi\rangle = \frac{1}{\sqrt{2}}[|\uparrow 1\rangle_i |\uparrow 0\rangle_j - |\uparrow 0\rangle_i |\uparrow 1\rangle_j]$$

$$(\mathbf{l}_i \cdot \mathbf{l}_j)|\psi\rangle = \frac{1}{\sqrt{2}}[|\uparrow 0\rangle_i |\uparrow 1\rangle_j - |\uparrow 1\rangle_i |\uparrow 0\rangle_j]$$

$$\langle\psi|(\mathbf{l}_i \cdot \mathbf{l}_j)|\psi\rangle = -1, \quad \langle\psi|(\mathbf{s}_i \cdot \mathbf{s}_j)|\psi\rangle = 1/4$$

$$\langle\psi|\hat{U}_{ij}|\psi\rangle = \frac{1}{2}\left[\langle\uparrow 1;\uparrow 0|\hat{U}_{ij}|\uparrow 1;\uparrow 0\rangle + \langle\uparrow 0;\uparrow 1|\hat{U}_{ij}|\uparrow 0;\uparrow 1\rangle - \langle\uparrow 1;\uparrow 0|\hat{U}_{ij}|\uparrow 0;\uparrow 1\rangle - \langle\uparrow 0;\uparrow 1|\hat{U}_{ij}|\uparrow 1;\uparrow 0\rangle\right] =$$
$$= \frac{1}{2}\big[F^0 A_0(1,0,1,0) + F^2 A_2(1,0,1,0) + F^0 A_0(0,1,0,1) + F^2 A_2(0,1,0,1) -$$
$$- F^0 A_0(1,0,0,1) - F^2 A_2(1,0,0,1) - F^0 A_0(0,1,1,0) - F^2 A_2(1,0,0,1)\big] = F^0 - (1/5)F^2$$

$$\lambda_0 + (1/4)\lambda_{ss} - \lambda_{ll} = F^0 - (1/5)F^2 \tag{35}$$

Solution of the system (33), (34) and (35):

$$\lambda_0 = F^0 - \frac{1}{5}F^2, \quad \lambda_{ss} = -\frac{12}{25}F^2, \quad \lambda_{ll} = -\frac{3}{25}F^2 \tag{36}$$

To express $\hat{H}_{int}$ in terms of the two-particle operator $\hat{U}_{ij}$ we use identities

$$\frac{1}{2}\sum_{i\neq j}\lambda_0 = \frac{\lambda_0}{2}\hat{N}(\hat{N}-1) \tag{37}$$

$$\frac{1}{2}\sum_{i\neq j}\lambda_{ss}(\mathbf{s}_i \cdot \mathbf{s}_j) = \frac{\lambda_{ss}}{2}\left(\sum_i \mathbf{s}_i\right)^2 - \frac{\lambda_{ss}}{2}\sum_i \mathbf{s}_i^2 = \frac{\lambda_{ss}}{2}\hat{S}^2 - \frac{\lambda_{ss}}{2}\hat{N}\frac{3}{4} \tag{38}$$

$$\frac{1}{2}\sum_{i\neq j}\lambda_{ll}(\mathbf{l}_i \cdot \mathbf{l}_j) = \frac{\lambda_{ll}}{2}\left(\sum_i \mathbf{l}_i\right)^2 - \frac{\lambda_{ll}}{2}\sum_i \mathbf{l}_i^2 = \frac{\lambda_{ll}}{2}\hat{L}^2 - \frac{\lambda_{ll}}{2}\hat{N}2 \tag{39}$$

Finally we get:

$$\hat{H}_{int} = -\left(\frac{\lambda_0}{2} + \frac{3}{8}\lambda_{ss} + \lambda_{ll}\right)\hat{N} + \frac{\lambda_0}{2}\hat{N}^2 + \frac{\lambda_{ss}}{2}\hat{S}^2 + \frac{\lambda_{ll}}{2}\hat{L}^2 \tag{40}$$

Or in the $U - J$ notation from the previous section $U \equiv F^0 + (4/25)F^2, J \equiv (3/25)F^2$

$$\hat{H}_{int} = \left(4J - \frac{U}{2}\right)\hat{N} + (U - 3J)\frac{\hat{N}^2}{2} - J\left[2\hat{S}^2 + \frac{\hat{L}^2}{2}\right] \tag{41}$$

The Hamiltonian with a chemical potential added:

$$\hat{H} = -\mu\hat{N} + \hat{H}_{int} = -(\mu - \mu_0)(\hat{N} - 3) + (U - 3J)\frac{(\hat{N} - 3)^2}{2} - J\left[2\hat{S}^2 + \frac{\hat{L}^2}{2}\right] + \text{const}, \tag{42}$$

where $\mu_0 = 5U/2 - 5J$ is the chemical potential corresponding to the half-filling.

This form allows to readily find all energy levels relying only on a classification of the eigenstates of the Hamiltonian with respect to the spin and orbital moments of the system:

$$E = -(\mu - \mu_0)(N - 3) + (U - 3J)\frac{(N - 3)^2}{2} - J\left[2S(S + 1) + \frac{L(L + 1)}{2}\right] \tag{43}$$

N	L	S	E	Degree of degeneracy $g = (2L + 1)(2S + 1)$
0	0	0	0	1
1	1	1/2	$-\mu$	6
2	2	0	$-2\mu + U - J$	5
2	1	1	$-2\mu + U - 3J$	9
2	0	0	$-2\mu + U + 2J$	1
3	2	1/2	$-3\mu + 3U - 6J$	10
3	1	1/2	$-3\mu + 3U - 4J$	6
3	0	3/2	$-3\mu + 3U - 9J$	4
4	2	0	$-4\mu + 6U - 11J$	5
4	1	1	$-4\mu + 6U - 13J$	9
4	0	0	$-4\mu + 6U - 8J$	1
5	1	1/2	$-5\mu + 10U - 20J$	6
6	0	0	$-6\mu + 15U - 30J$	1