# Expansion of a Wave Function in Terms of the Spherical Harmonics at a Different Site

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## 1. Introduction

We need very often the calculations of the matrix elements given by the two center integral in the solid state theory. The matrix elements are given by $\langle\phi|V|\psi\rangle$, in which $V$ is the operator of a physical quantity, and $\psi$ and $\phi$ are the atomic wave functions of an electron having the centers at the different positions given by $\boldsymbol{\lambda}$ and $\boldsymbol{\lambda}_0$, and therefore $\psi = \psi(\boldsymbol{r}-\boldsymbol{\lambda})$ and $\phi = \phi(\boldsymbol{r}-\boldsymbol{\lambda}_0)$. The positions specified by $\boldsymbol{\lambda}$ and $\boldsymbol{\lambda}_0$ are denoted by $A$ and $O$, respectively, and generally the position $O$ can be taken to be the origin ($\boldsymbol{\lambda}_0 = 0$). This matrix element is the two center integral since it includes the wave functions having the different centers. When $V$ is the difference between the atomic and the crystal periodic potentials, the matrix element means the overlap integral between the sites $A$ and $O$, and plays an important role for calculations of the band structure in LCAO method [1]. On the other hand, when $V$ is the momentum $\boldsymbol{p}$, it is the transition probability between the two states at the different sites in the absorption of a photon [2].

As is well known, an idea of calculating the matrix element given by the two center integral is to expand $\psi(\boldsymbol{r}-\boldsymbol{\lambda})$ and $\phi(\boldsymbol{r})$ in terms of the spherical harmonics centered at the origin. As a result of it, when $V$ is an operator with the s-symmetry, only the components of the spherical harmonics with the same $l$ and $m$ in the expansions of $\psi$ and $\phi$ can contribute to the matrix element, which leads to the selection rule of $\Delta l = 0$ and $\Delta m = 0$. For $V$ with the p-symmetry, the selection rule is $\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$. It is also easy to obtain the similar selection rules for $V$ with the other symmetries of such as d, f and so on. Therefore, the problem is to expand $\psi$ and $\phi$ around the origin in terms of the spherical harmonics. The expansion of $\phi$ is easy since the center coincides with the origin. However, the expansion of $\psi$ is not so easy because the center is deviated from the origin.

My aim in this note is to expand $\psi(\boldsymbol{r}-\boldsymbol{\lambda})$ around the origin using the spherical harmonics having the center there. Below, we adopt the two following assumptions. 1) $\psi(\boldsymbol{r})$ is in the $l$ state, in which the values of $l = 0, 1, 2, 3$ correspond to s, p, d and f states, respectively. 2) $\psi(\boldsymbol{r})$ is a linear combination of the spherical harmonics $Y_{lm}(\theta, \phi)$, which reflects the symmetry of the crystal field due to the surrounding ions. When the crystal has the cubic symmetry, $\psi(\boldsymbol{r})$ denotes one of the cubic harmonics for the given $l$.

## 2. Formulation

The four coordinate systems are needed to argue the expansion of $\psi(\boldsymbol{r}-\boldsymbol{\lambda})$. We put forward the argument by defining these coordinate systems in the suitable sequence. The first kind of the system, $O$-$xyz$, is an arbitrary system, in which the origin coincides with the position $O$. The vector $\boldsymbol{r}$ indicates the position of an electron in the $O$-$xyz$ system and $\boldsymbol{\lambda}$ denotes the position $A$ which is the center of the wavefunction $\psi$. We put $\boldsymbol{r} = (x, y, z) = r(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ and $\boldsymbol{\lambda} = \lambda(\sin\beta\cos\alpha, \sin\beta\sin\alpha, \cos\beta)$, in which $(r, \theta, \phi)$ and $(\lambda, \beta, \alpha)$ are the polar coordinates of $\boldsymbol{r}$ and $\boldsymbol{\lambda}$, respectively, in this system. The second kind of the coordinate system is that the origin is the position $A$ and each axis is parallel to the corresponding one in the $O$-$xyz$ system mentioned above. This system is denoted by $A$-$x'y'z'$. The vector $\boldsymbol{R}(= \boldsymbol{r}-\boldsymbol{\lambda})$ gives the position vector of the electron in this system. The polar coordinates $R$, $\theta'$ and $\phi'$ are defined by $\boldsymbol{R} = R(\sin\theta'\cos\phi'$, sin

$\theta' \sin\phi', \cos\theta')$. From the assumptions for the $\psi$ described in § 1, $\psi(\boldsymbol{R})$ is purely in the $l$ state in this system, and is given by

$$\psi(\boldsymbol{R}) = Q_l(R) \sum_{m=-l}^{l} a_{lm} Y_{lm}(\theta', \phi'), \tag{1}$$

where $Q_l(R)$ is the radial part, $Y_{lm}(\theta', \phi')$ is the spherical harmonics and $a_{lm}$ is the expansion coefficient. We use the definition in ref. [3] for $Y_{lm}(\theta, \phi)$ and it is given by

$$Y_{lm}(\theta, \phi) = \varepsilon_m k_{lm} P_l^m(\cos\theta) \frac{1}{\sqrt{2\pi}} \exp(im\phi), \tag{2}$$

$$\varepsilon_m = (-1)^{(m+|m|)/2}, \tag{3a}$$

$$k_{lm} = \sqrt{\frac{2l+1}{2} \cdot \frac{(l-|m|)!}{(l+|m|)!}} \tag{3b}$$

where $P_l^m(\cos\theta)$ is the associated Legendre function. The third kind of the coordinate system is made from the $O$-$xyz$ system in the following way. We rotate the $O$-$xyz$ system around the $z$-axis by the angle $\alpha$ and get the $O$-$\xi Yz$ system. Next, we rotate the $O$-$\xi Yz$ system around the $Y$-axis by $\beta$. The system obtained from these twice rotations is referred to as the $O$-$XYZ$, for which the direction of the $Z$-axis is in the same one as $\boldsymbol{\lambda}$. The polar coordinates of $\boldsymbol{r}$ in this system is given by $r$, $\Theta$ and $\Phi$.

The fourth kind of the system is obtained by the parallel movement of the $O$-$XYZ$ by $\boldsymbol{\lambda}$ and is denoted by the $A$-$X'Y'Z'$, in which the origin is the position $A$. The polar coordinates of $\boldsymbol{R}$ in this system are $R, \Theta'$ and $\Phi'$. Since each axis in the $A$-$X'Y'Z'$ is parallel to one in the $O$-$XYZ$, we obtain

$$\Phi = \Phi', \quad r\sin\Theta = R\sin\Theta' \tag{4}$$

$$R^2 = r^2 + \lambda^2 - 2\lambda r\cos\Theta, \tag{5a}$$

$$r^2 = R^2 + \lambda^2 + 2\lambda R\cos\Theta'. \tag{5b}$$

The relation between the $O$-$xyz$ and the $O$-$XYZ$ systems is very similar to the one between the $A$-$x'y'z'$ and the $A$-$X'Y'Z'$ systems.

The quantization axis in the representation of $Y_{lm}(\theta', \phi')$ in eq. (1) is chosen to be the $z'$-axis in the $A$-$x'y'z'$ system. Here we change the quantization axis to the $Z'$-axis in the $A$-$X'Y'Z'$ system. Then, as the basis set for the angular part of the wave function, the spherical harmonics $Y_{LM}(\Theta', \Phi')$ in the $A$-$X'Y'Z'$ system can be taken. Therefore, $Y_{lm}(\theta', \phi')$ can be represented by the linear combination of $Y_{lm'}(\Theta', \Phi')$ in the following way [3],

$$Y_{lm}(\theta', \phi') = \sum_{m'=-l}^{l} Y_{lm'}(\Theta', \Phi') R_{mm'}^{(l)}(\alpha\beta)^*, \tag{6}$$

$$R_{mm'}^{(l)}(\alpha\beta) = \langle lm|\exp(-i\alpha J_z)\exp(-i\beta J_y)|lm'\rangle = \exp(-i\alpha m) r_{mm'}^{(l)}(\beta), \tag{7}$$

$$r_{mm'}^{(l)}(\beta) = \langle lm|\exp(-i\beta J_y)|lm'\rangle$$
$$= \sum_t (-1)^t \frac{\sqrt{(l+m)!(l-m)!(l+m')!(l-m')!}}{(l+m-t)!(l-m'-t)!t!(t-m+m')!} \xi^{2l+m-m'-2t} \eta^{2t-m+m'} \tag{8}$$

where $R_{mm'}^{(l)}(\alpha\beta)$ is the rotation matrix, and $J_y$ and $J_z$ are the $y$ and $z$ components of the angular momentum operator, respectively, and the summation with respect to $t$ is carried out under the non-negative for all factorials and $\xi = \cos(\beta/2)$ and $\eta = \sin(\beta/2)$. The explicit forms of the matrices $r^{(l)}(\beta)$ for $l = 0, 1, 2, 3$ and 4 are given in Appendix A. Using eq. (6), eq. (1) can be written as follows,

$$\psi(\boldsymbol{R}) = \sum_{m=-l}^{l} \sum_{m'=-l}^{l} a_{lm} R_{mm'}^{(l)}(\alpha\beta)^* Q_l(R) Y_{lm'}(\Theta', \Phi'). \tag{9}$$

According to Löwdin [4], $Q_l(R) Y_{lm'}(\Theta', \Phi')$ in eq. (9) can be expanded using the spherical harmonics in the $O$-$XYZ$ system.

$$Q_l(R)Y_{lm'}(\Theta', \Phi') = \sum_{L=0}^{\infty}\sum_{M=-L}^{L} f^{(l)}_{Lm'M}(r, \lambda)Y_{LM}(\Theta, \Phi), \tag{10}$$

with

$$f^{(l)}_{Lm'M}(r, \lambda) = \int Q_l(R)Y_{lm'}(\Theta', \Phi')Y_{LM}(\Theta, \Phi)^* \sin\Theta \, d\Theta \, d\Phi. \tag{11}$$

For the integrations in eq. (11), we must use eqs. (4) and (5). Using $\Phi' = \Phi$ and eq. (2) and performing the $\Phi$-integral in eq. (11), we easily see that $f^{(l)}_{Lm'M}(r, \lambda)$ is not zero only for $m' = M$, and we can put $f^{(l)}_{Lm'M}(r, \lambda) = f^{(l)}_{Lm'}(r, \lambda)\delta_{m'M}$. Then, eqs. (10) and (11) become to

$$Q_l(R)Y_{lm'}(\Theta', \Phi') = \sum_{L=0}^{\infty} f^{(l)}_{Lm'}(r, \lambda)Y_{Lm'}(\Theta, \Phi), \tag{12}$$

$$f^{(l)}_{L\mu}(r, \lambda) = k_{l\mu}\, k_{L\mu} \int_0^{\pi} Q_l(R)P_l^{\mu}(\cos\Theta')P_L^{\mu}(\cos\Theta)\sin\Theta \, d\Theta, \tag{13a}$$

$$= \frac{k_{l\mu}\, k_{L\mu}}{\lambda r}\int_{|\lambda-r|}^{\lambda+r} dR\, R\, Q_l(R)P_l^{\mu}\left(\frac{r^2-R^2-\lambda^2}{2\lambda R}\right)P_L^{\mu}\left(\frac{r^2+\lambda^2-R^2}{2\lambda r}\right), \tag{13b}$$

where $f^{(l)}_{L\mu}(r, \lambda) = f^{(l)}_{L|\mu|}(r, \lambda)$ and $|\mu| \leqq \min(l, L)(= \Lambda)$. When $|\mu| \leqq \Lambda$ is not satisfied, $f^{(l)}_{L\mu}(r, \lambda) = 0$. Using eq. (12), eq. (9) becomes to

$$\psi(\boldsymbol{R}) = \sum_{m=-l}^{l}\sum_{m'=-\Lambda}^{\Lambda} a_{lm}R^{(l)}_{mm'}(\alpha\beta)^* \sum_{L=0}^{\infty} f^{(l)}_{Lm'}(r, \lambda)Y_{Lm'}(\Theta, \Phi). \tag{14}$$

Here we change again the quantization axis to the z-axis in the *O-xyz* system. Then, $Y_{Lm'}(\Theta, \Phi)$ can be expanded using the spherical harmonics in the *O-xyz* system, which is similar to eq. (6).

$$Y_{Lm'}(\Theta, \Phi) = \sum_{M=-L}^{L} Y_{LM}(\theta, \phi)R^{(L)}_{Mm'}(\alpha\beta). \tag{15}$$

Eq. (15) is inserted to eq. (14), then we obtain

$$\psi(\boldsymbol{r}-\boldsymbol{\lambda}) = \sum_{L=0}^{\infty}\sum_{M=-L}^{L} F^{(l)}_{LM}(r, \lambda)Y_{LM}(\theta, \phi), \tag{16}$$

$$F^{(l)}_{LM}(r, \lambda) = \sum_{m=-l}^{l}\sum_{m'=-\Lambda}^{\Lambda} a_{lm}\exp(i(m-M)\alpha)r^{(l)}_{mm'}(\beta)\, r^{(L)}_{Mm'}(\beta)\, f^{(l)}_{Lm'}(r, \lambda). \tag{17}$$

This is the final result for the expansion of $\psi(\boldsymbol{r}-\boldsymbol{\lambda})$.

## 3. Examples of expansions

In this section, we give the examples of the expansions for the wave functions $\psi(\boldsymbol{r}-\boldsymbol{\lambda})$ with the s and p symmetries.

1) $\psi_s(\boldsymbol{r}-\boldsymbol{\lambda})$

The wave function with the s-symmetry is assumed to be $\psi_s(\boldsymbol{r}-\boldsymbol{\lambda}) = Q_0(R)Y_{00}(\theta', \phi')$, in which $R$, $\theta'$ and $\phi'$ are the polar coordinates in the *A-x'y'z'* system. We use $a_{0m} = \delta_{m0}$ and the matrices $r^{(l)}_{mm'}(\beta)$ in Appendix A in eq. (17). The coefficients of $f^{(0)}_{L0}(r, \lambda)$ in $F^{(0)}_{LM}(r, \lambda)$ are tabulated for the states $Y_{LM}(\theta, \phi)$ ($= | LM >$) until $L = 4$ in Appendix B.

2) $\psi_{pm}(\boldsymbol{r}-\boldsymbol{\lambda})$ ($m = 0, \pm 1$)

The wave functions with the p-symmetry are given by $\psi_{pm}(\boldsymbol{r}-\boldsymbol{\lambda}) = Q_1(R)Y_{1m}(\theta', \phi')$ ($m = 0, \pm 1$), and therefore $a_{1\mu} = \delta_{\mu m}$ in eq. (17). The coefficients of $f^{(1)}_{Lm}(r, \lambda)$ $(m = 0, 1)$ in $F^{(1)}_{LM}(r, \lambda)$ are tabulated for the states $|LM>$ until $L = 4$ in Appendix C.

3) Energy integrals

The energy integrals $E_{u,v}$ introduced by Slater and Koster[1] are given by the matrix element $E_{u,v} = \langle\psi_u(\boldsymbol{r})|V(r)|\psi_v(\boldsymbol{r}-\boldsymbol{\lambda})\rangle$, in which $V(r)$ has the s-symmetry. When $\psi_u(\boldsymbol{r})$ and $\psi_v(\boldsymbol{r}-\boldsymbol{\lambda})$ are the cubic harmonics for the s and p states, $E_{u,v}$ are easily calculated using Appendices B and C. The results are in agreement with the ones by Slater and Koster [1, 5].

## 4. Summary

It has been considered that the atomic wavefunction centered at a different site from the origin is expanded using the spherical harmonics having the center at the origin. The general formula for the expansion is given, and the expanded forms until $L = 4$ for the s and p wavefunctions are tabulated.

## Appendix A: Rotation matrices $r^{(J)}(\beta)$ for $J = 0, 1, 2, 3$ and $4$

Using the relations for $r^{(J)}(\beta)$ given by $r^{(J)}_{MM'}(\beta) = r^{(J)}_{M'M}(-\beta) = (-1)^{M-M'}\, r^{(J)}_{-M-M'}(\beta)$ [3], the matrix elements which are not shown for the cases of $J = 3, 4$ can be easily calculated from the given ones.

$c = \cos\beta : s = \sin\beta$

0) $r^{(0)}(\beta) = 1$

1) $r^{(1)}_{MM'}(\beta)$

| $M \backslash M'$ | 1 | 0 | −1 |
|---|---|---|---|
| 1 | $(1+c)/2$ | $-\sqrt{2}s/2$ | $(1-c)/2$ |
| 0 | $\sqrt{2}s/2$ | $c$ | $-\sqrt{2}s/2$ |
| −1 | $(1-c)/2$ | $\sqrt{2}s/2$ | $(1+c)/2$ |

2) $r^{(2)}_{MM'}(\beta)$

| $M \backslash M'$ | 2 | 1 | 0 | −1 | −2 |
|---|---|---|---|---|---|
| 2 | $(1+c)^2/4$ | $-(1+c)s/2$ | $\sqrt{6}s^2/4$ | $-(1-c)s/2$ | $(1-c)^2/4$ |
| 1 | $(1+c)s/2$ | $-(1+c)(1-2c)/2$ | $-\sqrt{6}cs/2$ | $(1-c)(1+2c)/2$ | $-(1-c)s/2$ |
| 0 | $\sqrt{6}s^2/4$ | $\sqrt{6}cs/2$ | $-(1-3c^2)/2$ | $-\sqrt{6}cs/2$ | $\sqrt{6}s^2/4$ |
| −1 | $(1-c)s/2$ | $(1-c)(1+2c)/2$ | $\sqrt{6}cs/2$ | $-(1+c)(1-2c)/2$ | $-(1+c)s/2$ |
| −2 | $(1-c)^2/4$ | $(1-c)s/2$ | $\sqrt{6}s^2/4$ | $(1+c)s/2$ | $(1+c)^2/4$ |

3) $r^{(3)}_{MM'}(\beta)$

| $M \backslash M'$ | 3 | 2 | 1 | 0 |
|---|---|---|---|---|
| 3 | $(1+c)^3/8$ | | | |
| 2 | $\sqrt{6}(1+c)^2s/8$ | $-(1+c)^2(2-3c)/4$ | | |
| 1 | $\sqrt{15}(1+c)s^2/8$ | $-\sqrt{10}(1+c)(1-3c)s/8$ | $-(1+c)(1+10c-15c^2)/8$ | |
| 0 | $\sqrt{5}s^3/4$ | $\sqrt{30}cs^2/4$ | $\sqrt{3}(5c^2-1)s/4$ | $(5c^2-3)c/2$ |
| −1 | $\sqrt{15}(1-c)s^2/8$ | $\sqrt{10}(1-c)(1+3c)s/8$ | $-(1-c)(1-10c-15c^2)/8$ | |
| −2 | $\sqrt{6}(1-c)^2s/8$ | $(1-c)^2(2+3c)/4$ | | |
| −3 | $(1-c)^3/8$ | | | |

4) $r^{(4)}_{MM'}(\beta)$

| $M \backslash M'$ | 4 | 3 | 2 | 1 | 0 |
|---|---|---|---|---|---|
| 4 | $(1+c)^4/16$ | | | | |
| 3 | $\sqrt{2}(1+c)^3 s/8$ | $-(1+c)^3(3-4c)/8$ | | | |
| 2 | $\sqrt{7}(1+c)^2 s^2/8$ | $-\sqrt{14}(1+c)^2(1-2c)s/8$ | $(1+c)^2(1-7c+7c^2)/4$ | | |
| 1 | $\sqrt{14}(1+c)s^3/8$ | $-\sqrt{7}(1+c)(1-4c)s^2/8$ | $-\sqrt{2}(1+c)(1+7c-14c^2)s/8$ | $(1+c)(3-6c-21c^2+28c^3)/8$ | |
| 0 | $\sqrt{70}s^4/16$ | $\sqrt{35}cs^3/4$ | $\sqrt{10}(7c^2-1)s^2/8$ | $\sqrt{5}(7c^2-3)cs/4$ | $(35c^4-30c^2+3)/8$ |
| −1 | $\sqrt{14}(1-c)s^3/8$ | $\sqrt{7}(1-c)(1+4c)s^2/8$ | $-\sqrt{2}(1-c)(1-7c-14c^2)s/8$ | $-(1-c)(3+6c-21c^2-28c^3)/8$ | |
| −2 | $\sqrt{7}(1-c)^2 s^2/8$ | $\sqrt{14}(1-c)^2(1+2c)s/8$ | $(1-c)^2(1+7c+7c^2)/4$ | | |
| −3 | $\sqrt{2}(1-c)^3 s/8$ | $(1-c)^3(3+4c)/8$ | | | |
| −4 | $(1-c)^4/16$ | | | | |

**Appendix B: Expansion of the s-wavefunction $\psi_s(r-\lambda)$.**

The coefficients of $f^{(0)}_{LO}(r, \lambda)$ in $F^{(0)}_{LM}(r, \lambda)$ are shown for the states $Y_{LM}(\theta, \phi)$ $(= |LM\rangle)$. $(l, m, n) = (\sin\beta \cos\alpha, \sin\beta \sin\alpha, \cos\beta)$ : $X_{\pm} = l \pm im$ : $f_{LO} = f^{(0)}_{LO}(r, \lambda)$

| $\psi_s(r-\lambda)$ | | | | | | |
|---|---|---|---|---|---|---|
| $L=0$ | | $\|0\rangle$ | | | | |
| | $f_{00}$ | 1 | | | | |
| $L=1$ | | $\|1\rangle$ | $\|0\rangle$ | $\|-1\rangle$ | | |
| | $f_{10}$ | $-\sqrt{2}X_-/2$ | $n$ | $\sqrt{2}X_+/2$ | | |
| $L=2$ | | $\|2\rangle$ | $\|1\rangle$ | $\|0\rangle$ | $\|-1\rangle$ | $\|-2\rangle$ |
| | $f_{20}$ | $\sqrt{6}X_-^2/4$ | $-\sqrt{6}nX_-/2$ | $(3n^2-1)/2$ | $\sqrt{6}nX_+/2$ | $\sqrt{6}X_+^2/4$ |
| $L=3$ | | $\|3\rangle$ | $\|2\rangle$ | $\|1\rangle$ | $\|0\rangle$ | $\|-1\rangle$ |
| | $f_{30}$ | $-\sqrt{5}X_-^3/4$ | $\sqrt{30}nX_-^2/4$ | $-\sqrt{5}(5n^2-1)X_-/4$ | $n(5n^2-3)/2$ | $\sqrt{5}(5n^2-1)X_+/4$ |
| | | $\|-2\rangle$ | $\|-3\rangle$ | | | |
| | $f_{30}$ | $\sqrt{30}nX_+^2/4$ | $\sqrt{5}X_+^3/4$ | | | |
| $L=4$ | | $\|4\rangle$ | $\|3\rangle$ | $\|2\rangle$ | $\|1\rangle$ | $\|0\rangle$ |
| | $f_{40}$ | $\sqrt{70}X_-^4/16$ | $-\sqrt{35}nX_-^3/4$ | $\sqrt{10}(7n^2-1)X_-^2/8$ | $-\sqrt{5}n(7n^2-3)X_-/4$ | $(35n^4-30n^2+3)/8$ |
| | | $\|-1\rangle$ | $\|-2\rangle$ | $\|-3\rangle$ | $\|-4\rangle$ | |
| | $f_{40}$ | $\sqrt{5}n(7n^2-3)X_+/4$ | $\sqrt{10}(7n^2-1)X_+^2/8$ | $\sqrt{35}nX_+^3/4$ | $\sqrt{70}X_+^4/16$ | |

**Appendix C: Expansions of the p-wavefunctions $\psi_{pm}(r-\lambda)$ $(m = 0, \pm 1)$.**

The coefficients of $f^{(1)}_{L0}(r, \lambda)$ and $f^{(1)}_{L1}(r, \lambda)$ *in* $F^{(1)}_{LM}(r, \lambda)$ are shown for the states $Y_{LM}(\theta, \phi)$ $(= |LM>)$. $(l, m, n) = (\sin\beta\cos\alpha, \sin\beta\sin\alpha, \cos\beta)$ : $X_\pm = l \pm im$ : $f_{Lm} = f^{(1)}_{Lm}(r, \lambda)$

1) $\psi_{p1}(r-\lambda)$

| | | | | | | |
|---|---|---|---|---|---|---|
| $L=0$ | | $\|0>$ | | | | |
| | $f_{00}$ | $-\sqrt{2}X_+/2$ | | | | |
| $L=1$ | | $\|1>$ | $\|0>$ | $\|-1>$ | | |
| | $f_{10}$ | $(1-n^2)/2$ | $-\sqrt{2}nX_+/2$ | $-X_+^2/2$ | | |
| | $f_{11}$ | $(1+n^2)/2$ | $\sqrt{2}nX_+/2$ | $X_+^2/2$ | | |
| $L=2$ | | $\|2>$ | $\|1>$ | $\|0>$ | $\|-1>$ | $\|-2>$ |
| | $f_{20}$ | $-\sqrt{3}(1-n^2)X_-/4$ | $\sqrt{3}n(1-n^2)/2$ | $\sqrt{2}(1-3n^2)X_+/4$ | $-\sqrt{3}nX_+^2/2$ | $-\sqrt{3}X_+^3/4$ |
| | $f_{21}$ | $-(1+n^2)X_-/2$ | $n^3$ | $\sqrt{6}n^2X_+/2$ | $nX_+^2$ | $X_+^3/2$ |
| $L=3$ | | $\|3>$ | $\|2>$ | $\|1>$ | $\|0>$ | $\|-1>$ |
| | $f_{30}$ | $\sqrt{10}(1-n^2)X_-^2/8$ | $-\sqrt{15}n(1-n^2)X_-/4$ | $\sqrt{6}(5n^2-1)(1-n^2)/8$ | $-\sqrt{2}n(5n^2-3)X_+/4$ | $-\sqrt{6}(5n^2-1)X_+^2/8$ |
| | $f_{31}$ | $\sqrt{15}(1+n^2)X_-^2/8$ | $-\sqrt{10}n(1+3n^2)X_-/8$ | $-(1+6n^2-15n^4)/8$ | $\sqrt{3}n(5n^2-1)X_+/4$ | $-(1-15n^2)X_+^2/8$ |
| | | $\|-2>$ | $\|-3>$ | | | |
| | $f_{30}$ | $-\sqrt{15}nX_+^3/4$ | $-\sqrt{10}X_+^4/8$ | | | |
| | $f_{31}$ | $3\sqrt{10}nX_+^3/8$ | $\sqrt{15}X_+^4/8$ | | | |
| $L=4$ | | $\|4>$ | $\|3>$ | $\|2>$ | $\|1>$ | $\|0>$ |
| | $f_{40}$ | $-\sqrt{35}(1-n^2)X_-^3/16$ | $\sqrt{70}n(1-n^2)X_-^2/8$ | $-\sqrt{5}(7n^2-1)(1-n^2)X_-/8$ | $\sqrt{10}n(1-n^2)(7n^2-3)/8$ | $-\sqrt{2}(35n^4-30n^2+3)X_+/16$ |
| | $f_{41}$ | $-\sqrt{14}(1+n^2)X_-^3/8$ | $\sqrt{7}n(1+2n^2)X_-^2/4$ | $\sqrt{2}(1+n^2-14n^4)X_-/8$ | $n^3(7n^2-5)/2$ | $\sqrt{5}n^2(7n^2-3)X_+/4$ |
| | | $\|-1>$ | $\|-2>$ | $-3>$ | $\|-4>$ | |
| | $f_{40}$ | $-\sqrt{10}n(7n^2-3)X_+^2/8$ | $-\sqrt{5}(7n^2-1)X_+^3/8$ | $-\sqrt{70}nX_+^4/8$ | $-\sqrt{35}X_+^5/16$ | |
| | $f_{41}$ | $-n(3-14n^2)X_+^2/4$ | $-\sqrt{2}(1-14n^2)X_+^3/8$ | $\sqrt{7}nX_+^4/2$ | $\sqrt{14}X_+^5/8$ | |

2) $\psi_{p0}(\boldsymbol{r}-\boldsymbol{\lambda})$

| | | | | | | |
|---|---|---|---|---|---|---|
| $L=0$ | | $\vert 0\rangle$ | | | | |
| | $f_{00}$ | $n$ | | | | |
| $L=1$ | | $\vert 1\rangle$ | $\vert 0\rangle$ | $\vert -1\rangle$ | | |
| | $f_{10}$ | $-\sqrt{2}nX_-/2$ | $n^2$ | $\sqrt{2}nX_+/2$ | | |
| | $f_{11}$ | $\sqrt{2}nX_-/2$ | $1-n^2$ | $-\sqrt{2}nX_+/2$ | | |
| $L=2$ | | $\vert 2\rangle$ | $\vert 1\rangle$ | $\vert 0\rangle$ | $-1\rangle$ | $\vert -2\rangle$ |
| | $f_{20}$ | $\sqrt{6}nX_-^2/4$ | $-\sqrt{6}n^2X_-/2$ | $-n(1-3n^2)/2$ | $\sqrt{6}n^2X_+/2$ | $\sqrt{6}nX_+^2/4$ |
| | $f_{21}$ | $-\sqrt{2}nX_-^2/2$ | $-\sqrt{2}(1-2n^2)X_-/2$ | $\sqrt{3}n(1-n^2)/2$ | $\sqrt{2}(1-2n^2)X_+/2$ | $-\sqrt{2}nX_+^2/2$ |
| $L=3$ | | $\vert 3\rangle$ | $\vert 2\rangle$ | $\vert 1\rangle$ | $\vert 0\rangle$ | $\vert -1\rangle$ |
| | $f_{30}$ | $-\sqrt{5}nX_-^3/4$ | $\sqrt{30}n^2X_-^2/4$ | $-\sqrt{3}n(5n^2-1)X_-/4$ | $n^2(5n^2-3)/2$ | $\sqrt{3}n(5n^2-1)X_+/4$ |
| | $f_{31}$ | $\sqrt{30}nX_-^3/8$ | $\sqrt{5}(1-3n^2)X_-^2/4$ | $-\sqrt{2}n(11-15n^2)X_-/8$ | $\sqrt{6}(1-n^2)(5n^2-1)/4$ | $\sqrt{2}n(11-15n^2)X_+/8$ |
| | | $\vert -2\rangle$ | $\vert -3\rangle$ | | | |
| | $f_{30}$ | $\sqrt{30}n^2X_+^2/4$ | $\sqrt{5}nX_+^3/4$ | | | |
| | $f_{31}$ | $\sqrt{5}(1-3n^2)X_+^2/4$ | $-\sqrt{30}nX_+^3/8$ | | | |
| $L=4$ | | $\vert 4\rangle$ | $\vert 3\rangle$ | $\vert 2\rangle$ | $\vert 1\rangle$ | $\vert 0\rangle$ |
| | $f_{40}$ | $\sqrt{70}nX_-^4/16$ | $-\sqrt{35}n^2X_-^3/4$ | $\sqrt{10}n(7n^2-1)X_-^2/8$ | $-\sqrt{5}n^2(7n^2-3)X_-/4$ | $n(35n^4-30n^2+3)/8$ |
| | $f_{41}$ | $-\sqrt{7}nX_-^4/4$ | $-\sqrt{14}(1-4n^2)X_-^3/8$ | $n(4-7n^2)X_-^2/2$ | $\sqrt{2}(3-27n^2+28n^4)X_-/8$ | $\sqrt{10}n(1-n^2)(7n^2-3)/4$ |
| | | $\vert -1\rangle$ | $\vert -2\rangle$ | $\vert -3\rangle$ | $\vert -4\rangle$ | |
| | $f_{40}$ | $\sqrt{5}n^2(7n^2-3)X_+/4$ | $\sqrt{10}n(7n^2-1)X_+^2/8$ | $\sqrt{35}n^2X_+^3/4$ | $\sqrt{70}nX_+^4/16$ | |
| | $f_{41}$ | $-\sqrt{2}(3-27n^2+28n^4)X_+/8$ | $n(4-7n^2)X_+^2/2$ | $\sqrt{14}(1-4n^2)X_+^3/8$ | $-\sqrt{7}nX_+^4/4$ | |

3) $\psi_{P_z-1}(r-\lambda)$

| | | | | | | |
|---|---|---|---|---|---|---|
| $L=0$ | | $\vert 0\rangle$ | | | | |
| | $f_{00}$ | $\sqrt{2}X_-/2$ | | | | |
| $L=1$ | | $\vert 1\rangle$ | $\vert 0\rangle$ | $\vert -1\rangle$ | | |
| | $f_{10}$ | $-X_-^2/2$ | $\sqrt{2}nX_-/2$ | $(1-n^2)/2$ | | |
| | $f_{11}$ | $X_-^2/2$ | $-\sqrt{2}nX_-/2$ | $(1+n^2)/2$ | | |
| $L=2$ | | $\vert 2\rangle$ | $\vert 1\rangle$ | $\vert 0\rangle$ | $\vert -1\rangle$ | $\vert -2\rangle$ |
| | $f_{20}$ | $\sqrt{3}X_-^3/4$ | $-\sqrt{3}nX_-^2/2$ | $-\sqrt{2}(1-3n^2)X_-/4$ | $\sqrt{3}n(1-n^2)/2$ | $\sqrt{3}(1-n^2)X_+/4$ |
| | $f_{21}$ | $-X_-^3/2$ | $nX_-^2$ | $-\sqrt{6}n^2X_-/2$ | $n^3$ | $(1+n^2)X_+/2$ |
| $L=3$ | | $\vert 3\rangle$ | $\vert 2\rangle$ | $\vert 1\rangle$ | $\vert 0\rangle$ | $\vert -1\rangle$ |
| | $f_{30}$ | $-\sqrt{10}X_-^4/8$ | $\sqrt{15}nX_-^3/4$ | $-\sqrt{6}(5n^2-1)X_-^2/8$ | $\sqrt{2}n(5n^2-3)X_-/4$ | $\sqrt{6}(5n^2-1)(1-n^2)/8$ |
| | $f_{31}$ | $\sqrt{15}X_-^4/8$ | $-3\sqrt{10}nX_-^3/8$ | $-(1-15n^2)X_-^2/8$ | $-\sqrt{3}n(5n^2-1)X_-/4$ | $-(1+6n^2-15n^4)/8$ |
| | | $\vert -2\rangle$ | $\vert -3\rangle$ | | | |
| | $f_{30}$ | $\sqrt{15}n(1-n^2)X_+/4$ | $\sqrt{10}(1-n^2)X_+^2/8$ | | | |
| | $f_{31}$ | $\sqrt{10}n(1+3n^2)X_+/8$ | $\sqrt{15}(1+n^2)X_+^2/8$ | | | |
| $L=4$ | | $\vert 4\rangle$ | $\vert 3\rangle$ | $\vert 2\rangle$ | $\vert 1\rangle$ | $\vert 0\rangle$ |
| | $f_{40}$ | $\sqrt{35}X_-^5/16$ | $-\sqrt{70}nX_-^4/8$ | $\sqrt{5}(7n^2-1)X_-^3/8$ | $-\sqrt{10}n(7n^2-3)X_-^2/8$ | $\sqrt{2}(35n^4-30n^2+3)X_-/16$ |
| | $f_{41}$ | $-\sqrt{14}X_-^5/8$ | $\sqrt{7}nX_-^4/2$ | $\sqrt{2}(1-14n^2)X_-^3/8$ | $-n(3-14n^2)X_-^2/4$ | $-\sqrt{5}n^2(7n^2-3)X_-/4$ |
| | | $\vert -1\rangle$ | $\vert -2\rangle$ | $\vert -3\rangle$ | $\vert -4\rangle$ | |
| | $f_{40}$ | $\sqrt{10}n(1-n^2)(7n^2-3)/8$ | $\sqrt{5}(7n^2-1)(1-n^2)X_+/8$ | $\sqrt{70}n(1-n^2)X_+^2/8$ | $\sqrt{35}(1-n^2)X_+^3/16$ | |
| | $f_{41}$ | $n^3(7n^2-5)/2$ | $-\sqrt{2}(1+n^2-14n^4)X_+/8$ | $\sqrt{7}n(1+2n^2)X_+^2/4$ | $\sqrt{14}(1+n^2)X_+^3/8$ | |

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