IOP Concise Physics

Elements of Photoionization Quantum Dynamics Methods

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Appendix A

Mathematical formalism

A.1 Solutions of the Laplace operator

The Laplace eigenvalue problem of the kinetic operator $\hat{K} = -\nabla^2/2$ (also known as the Helmholtz equation in a different context) is expressed as

$$(\nabla^2 + \mathbf{k}^2)\phi_{\mathbf{k}}(\mathbf{r}) = 0 \quad \rightarrow \quad \phi_{\mathbf{k}} = Ce^{\pm\imath\mathbf{kr}}, \tag{A.1}$$

with $\phi_{\mathbf{k}}(\mathbf{r})$ a special solution, known as a *plane wave*, and C a normalization constant. The spectrum is real, continuous from 0 to ∞. The choice of the normalization constant as $C = 1/(2\pi)^{3/2}$ fixes a Dirac-delta function δ orthonormalization of the plane waves,

$$\int \mathbf{d}\mathbf{r}\phi^*_{\mathbf{k}}(\mathbf{r})\phi_{\mathbf{k}'}(\mathbf{r}) = \delta(\mathbf{k}' - \mathbf{k}) \quad \longleftrightarrow \quad \int \mathbf{d}k\phi^*_{\mathbf{k}}(\mathbf{r}')\phi_{\mathbf{k}}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}'). \tag{A.2}$$

The spherical Bessel functions result as the radial part of the Laplace eigenvalue problem, when the solution $\phi_{\mathbf{k}}(\mathbf{r})$ is expanded on the spherical harmonics (SH) basis. This is immediately evident if one considers that for any two vectors $\mathbf{k} = (k, \vartheta, \varphi)$ and $\mathbf{r} = (r, \theta, \phi)$ we have

$$e^{\imath\mathbf{kr}} = \sum_l \sqrt{4\pi(2l + 1)}\,\imath^l j_l(kr)\, Y_{l0}(\Theta), \qquad \hat{k}\hat{r} = \cos\Theta, \tag{A.3}$$

with $j_l(kr)$ the spherical Bessel functions and Y_{lm} the SH functions.

Spherical Bessel functions. The asymptotic behaviour at the infinity of $j_l(kr)$ and its (irregular) twin, $\eta_l(kr)$, is of special interest:

$$j_l(kr) \longrightarrow \frac{\sin(kr - l\pi/2)}{kr}, \qquad \eta_l(kr) \longrightarrow -\frac{\cos(kr - l\pi/2)}{kr}. \tag{A.4}$$

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A.1.1 Spherical harmonics, angular basis of ∇^2

In the following, we assume that $Y_{lm} = Y_{lm}(\theta, \phi)$. The orthonormality relation is given by

$$\langle lm|l'm'\rangle = \int_0^{\pi} d\phi \int_0^{2\pi} \sin\theta \, d\theta \; Y^{\star}_{lm}(\theta, \phi) Y_{l'm'}(\theta, \phi) = \delta_{ll'}\delta_{mm'}. \tag{A.5}$$

The SH of $m = 0$ are related to the Legendre polynomials by

$$Y_{l0}(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi}} P_l(\cos\theta). \tag{A.6}$$

Upon applying the inversion operation $\mathbf{r} = (r, \theta, \phi) \to -\mathbf{r} = (r, \pi - \theta, \phi + \pi)$, the sign reversal of m and complex conjugation of the following relations are useful:

$$Y_{lm}(\theta - \pi, \phi + \pi) = (-)^l Y_{lm}, \qquad Y^*_{lm} = Y_{lm}(\theta, -\phi) = (-1)^m Y_{l-m}, \tag{A.7}$$

$$\cos\theta \; Y_{lm} = \kappa_{l+1,m} Y_{l+1m} + \kappa_{l,m} Y_{l-1m}, \tag{A.8a}$$

$$\sin\theta \frac{\partial}{\partial\theta} Y_{lm} = l\kappa_{l+1,m} Y_{l+1m} - (l+1)\kappa_{l,m} Y_{l-1m}, \tag{A.8b}$$

with

$$\kappa_{l,m} = \sqrt{\frac{l^2 - m^2}{4l^2 - 1}}. \tag{A.9}$$

Coulomb field on SH. For two arbitrary vectors, $\mathbf{r}$ and $\mathbf{r}'$, the following multipole expansion holds:

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \frac{4\pi}{2L+1} \frac{r_<^L}{r_>^{L+1}} Y^*_{LM}(\theta', \phi') Y_{LM}(\theta, \phi). \tag{A.10}$$

Clebsch–Gordan, Wigner-3*j* and Gaunt coefficients. The Gaunt coefficient is defined as the integral of three spherical harmonics:

$$G^{LM}_{l_am_a;l_bm_b} = \langle l_am_a \mid LM \mid l_bm_b\rangle = (-1)^{m_a} \sqrt{\frac{[L]}{4\pi}} \chi^{l_aLl_b}_{000} \chi^{l_aLl_b}_{-m_aMm_b}, \tag{A.11}$$

$$\chi^{j_1j_2j_3}_{m_1m_2m_3} = \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}, \tag{A.12}$$

where $[l] \equiv 2l + 1$. The Gaunt coefficient is of great physical importance as it is directly related to the angular part of the transition amplitudes between quantum mechanical states. It is equally important in radiation, quantum collision theory and atomic structure theory. The Gaunt factor is expressed in terms of the so-called Wigner-3j coefficient (χ)

symbols and the Clebsch–Gordan coefficients[1], $C^{j_1 j_2 j_3}_{m_1,m_2,m_3} = (-)^{j_2 - j_1 - m_3}\sqrt{[j_3]}\chi^{j_1 j_2 j_3}_{m_1 m_2,-m_3}$. Some important properties of the Wigner-3j symbol are given as follows:

$$\chi^{j_1 j_2 j_3}_{m_1 m_2 m_3} = (-)^{\Sigma}\chi^{j_2 j_1 j_3}_{m_2 m_1 m_3} = (-)^{\Sigma}\chi^{j_1 j_2 j_3}_{-m_1,-m_2,-m_3} = \chi^{j_2 j_3 j_1}_{m_2 m_3 m_1} \tag{A.13}$$

$$\chi^{j_1 j_2 j_3}_{m_1 m_2 m_3} \neq 0, \qquad |j_1 - j_2| \leqslant j \leqslant j_1 + J_2, \quad m_1 + m_2 = m. \tag{A.14}$$

For dipole transitions the following formula proves useful:

$$\begin{pmatrix} l_a & 1 & l_a + 1 \\ -m_a & 0 & m_b \end{pmatrix} = (-)^{l_a - m_a - 1}\sqrt{\frac{(l_a + 1)^2 - m_a^2}{(2l_a + 1)(l_a + 1)(2l_a + 3)}}. \tag{A.15}$$

Product of two SH at the same angles.

$$Y^*_{l_a m_a} Y_{l_b m_b} = \sum_{L=|l_a - l_b|}^{l_a + l_b} \sum_{M=-L}^{L} (-1)^M G^{l_b m_b}_{l_a, m_a; LM} Y_{LM} \tag{A.16}$$

$$Y_{l0} Y_{l'0} = \sum_{L=|l-l'|}^{l+l'} \sqrt{\frac{[l][l'][L]}{4\pi}} \begin{pmatrix} l & l' & L \\ 0 & 0 & 0 \end{pmatrix}^2 Y_{L0}. \tag{A.17}$$

Another useful relation is

$$\sum_{m=-l}^{l} Y^*_{lm}(\theta', \phi') Y_{l'm}(\theta, \phi) = \frac{2l + 1}{4\pi} Y_{l0}(\Theta, \Phi) = P_l(\cos\Theta), \tag{A.18}$$

where Θ is the angle between the directions along (θ', ϕ') and (θ, ϕ).

A.2 Integro-differential calculus formulas

Highly oscillating integrals and Dirac-delta function A formal definition of the Dirac-delta function in the $\mathbf{k}-\mathbf{r}$ space is obtained if in equation (A.2) we take $\mathbf{r}' = 0$:

$$\delta(\mathbf{r}) = \frac{1}{(2\pi)^3}\int \mathbf{dk} e^{\imath \mathbf{kr}} \quad \longleftrightarrow \quad \int \mathbf{dk}\delta(\mathbf{r} - \mathbf{r}')f(\mathbf{r}) = f(\mathbf{r}'), \tag{A.19}$$

with $f(\mathbf{r})$ any arbitrary function[2]. For our purposes the one-dimensional Dirac-delta function in the $\omega - t$ time–frequency plane can be defined by

[1] In the physics literature the Clebsch–Gordan coefficients are used as well (frequently as synonyms for the Wigner-3j coefficient). However the Wigner-3j symbols have higher symmetry than the Clebsch–Gordan coefficients.

[2] In fact, it is often defined by this second property alone and it should be noted that expressions containing the Dirac-delta inside integrals have the traditional properties of an any regular function.

$$\delta(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\ e^{\imath\omega t}$$
$$\int_{\omega_1}^{\omega_2} d\omega\ \delta(\omega-\omega_0)f(\omega) = f(\omega_0), \quad \omega_1 < \omega_0 < \omega_2. \tag{A.20}$$

So, essentially, the practical consequence of the delta function is to pick one and only one value of the function, $f(\omega_0)$, under the integral. The above definition can also be thought of as the limiting case of a finite-time integral which plays important role in the formulation [1],

$$\zeta_{\pm}(\omega, t_0) = -\imath\int_{t_0}^{t\to\infty} dt' e^{\pm\imath\omega t'} = \lim_{\eta\to 0}\frac{1}{\omega \pm \imath\eta}$$
$$= \begin{cases} \mathcal{P}\left[\frac{1}{\omega}\right] \mp \imath\pi\delta(\omega), & t_0 = 0, \\ \mp 2\pi\imath\delta(\omega), & t_0 = -t \end{cases}. \tag{A.21}$$

With this finite-time form of the Dirac-delta function two useful forms may be proven:

$$\int_{\omega_1}^{\omega_2} d\omega\ \zeta_{\pm}(\omega-\omega_0, t_0)f(\omega)$$
$$= \begin{cases} \mathcal{P}\int_{\omega_1}^{\omega_2} d\omega\frac{f(\omega)}{\omega-\omega_0} \mp \imath\pi f(\omega_0) & t_0 = 0, \\ \mp 2\pi\imath f(\omega_0), & t_0 = -t, \end{cases} \quad \omega_1 < \omega_0 < \omega_2. \tag{A.22}$$

If ω_0 is not included in the interval $[\omega_1, \omega_2]$ then only the principal value integral survives. Because of the symmetrical appearance of ω and t in the exponent of equation (A.21), the last two formulas hold by swapping t and ω accordingly and choosing proper integral limits. Finally, at this point we may define the Fourier transform (FT) and its inverse of a function as

$$F(\omega) = \int_{-\infty}^{\infty} dt\, f(t)e^{\imath\omega t} \quad \leftrightarrow \quad f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\ F(\omega)e^{-\imath\omega t}. \tag{A.23}$$

The prefactor 2π may appear different in other definitions of the FT.

Multivariate Taylor expansion. Based on the following general Taylor-like expansion for a multivariate function, $\psi(\mathbf{x})$, where $\mathbf{x} = (x_1, x_2, \ldots, x_k)$ and $d\mathbf{x} = (dx_1, dx_2, \ldots, dx_k)$:

$$\psi(\mathbf{x} + \mathbf{dx}) = \sum_n\left[\frac{1}{n!}\left(\sum_{i=1}^{k}\left(dx_i\frac{\partial}{\partial x_i}\right)\psi(\mathbf{x})\right)\right],$$

for functions of $\mathbf{r}$, t we have

$$\psi(\mathbf{r} + \mathbf{dr},\, t + dt) = \sum_n \frac{1}{n!}\left(\mathbf{dr} \cdot \nabla + dt\frac{\partial}{\partial t}\right)^n f(\mathbf{r},\, t) = e^{\mathbf{dr}\cdot\nabla + dt\frac{\partial}{\partial t}}\psi(\mathbf{r},\, t). \tag{A.24}$$

The above exponential form of the Taylor expansion immediately implies the generators of the spatial and time variations as the corresponding first-order differential operators.

Differentiation under the integral sign: Leibniz integration rule.

$$\begin{aligned}\int_{b(x)}^{a(x)} dx' F(x,\, x') &= F(x,\, b)b'(x) - F(x,\, a)a'(x) \\ &\quad + \int_{b(x)}^{a(x)} dx' \frac{\partial}{\partial x} F(x,\, x').\end{aligned} \tag{A.25}$$

A.3 Operator and (matrix) algebraic functionals

We may construct a function of an arbitrary operator, $\hat{B}$, using a power series expansion:

$$f(\hat{B}) = \sum_n c_n \hat{B}^n \quad \Longrightarrow \quad f(b_n) = \sum_n c_n b^n.$$

The c_n quantities are ordinary (possibly complex) numbers, also called c-numbers (non-operators). It is reasonable to assume that, if the above approach of expressing functions of operators is valid, the operator power expansion should converge upon replacing $\hat{B}$ with any of its eigenvalues ($\hat{B}\mathbf{x} = b\mathbf{x}$).

Among the most frequently encountered functions is the exponential one which, according to the above expansion, is defined by

$$e^{\hat{B}} = \sum_n \frac{1}{n!}\hat{B}^n,$$

where we have used the known expansion of the exponential function for c-numbers, $\exp(x) = \sum_n x^n/n!$.

Let us for now assume two non-commuting operators, $\hat{A}$ and $\hat{B}$, and z as a c-number parameter. The following useful identities hold between them:

$$e^{z\hat{A}}\hat{B}^n e^{-z\hat{A}} = (e^{z\hat{A}}\hat{B}e^{-z\hat{A}})^n, \qquad \hat{A}f(\hat{B})\hat{A}^{-1} = f(\hat{A}\hat{B}\hat{A}^{-1}), \tag{A.26}$$

$$e^{z\hat{A}}\hat{B}e^{-z\hat{A}} = \hat{B} + z[\hat{A},\, \hat{B}] + \frac{z^2}{2!}[\hat{A},\, [\hat{A},\, \hat{B}]] + \frac{z^3}{3!}[\hat{A},\; [\hat{A},\; [\hat{A},\, \hat{B}]]] + \cdots. \tag{A.27}$$

Another very useful formula is a special case of the so-called Baker–Campbell–Hausdorff theorem[3]:

[3] The theorem provides the solution to equation $e^{\hat{C}} = e^{\hat{A}}e^{\hat{B}}$ for $\hat{C}$, where $\hat{A}$ and $\hat{B}$ are non-commuting operators.

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\hat{B}}e^{-\frac{1}{2}[\hat{A},\,\hat{B}]} = e^{\hat{B}}e^{\hat{A}}e^{\frac{1}{2}[\hat{A},\,\hat{B}]}, \qquad [\hat{A}, [\hat{A}, \hat{B}]] = [\hat{B}, [\hat{A}, \hat{B}]] = 0. \tag{A.28}$$

The above relation can be extended for the case of arbitrary, constant and non-commuting operators, $\hat{A}$ and $\hat{B}$, by

$$e^{\hat{A}+\hat{B}} = e^{\hat{A}}e^{\int_0^1 dt e^{-t\hat{A}}\hat{B}e^{t\hat{A}}}. \tag{A.29}$$

The above theorem is a limiting case of the disentangling theorem for non-commuting operators, first presented by Feynman in [2, 3]. A thorough presentation of operator algebra can also be found in the book of Louissel [4].

By representing an operator on a finite basis we end up with a matrix-based algebra. An algebra of this kind is very well suited to implementing the computational algorithms required for the solution of differential equations. For example, consider the following problem:

$$\dot{\mathbf{y}} = \mathbf{A}(t)\mathbf{y}(t) + \mathbf{F}(t), \qquad \mathbf{y}(t_0) = \mathbf{y}_0, \tag{A.30}$$

where $\mathbf{y}^T(t) = (\mathbf{y}_1(t), \mathbf{y}_2(t), \dots, \mathbf{y}_N(t))$ is a vector containing the unknown time-dependent (TD) coefficients. Matrix $\mathbf{A}$ may be TD or constant. If it is constant then we have the formal solution

$$\mathbf{y}(t) = e^{\mathbf{A}(t-t_0)}\mathbf{y}(0) + \int_{t_0}^{t} dt' e^{\mathbf{A}(t-t')}\mathbf{F}(t'). \tag{A.31}$$

If it is not, then we may obtain the solution of (A.30) by repeatedly solving its *short-time* approximation. For example, we assume $\mathbf{F}(t) = 0$. We then divide the total time interval into k smaller time intervals, $[t_j, t_j + \tau_j]$, $j = 1, 2, \dots, k$, such that $\mathbf{A}(t)$ can be regarded as approximately constant $A(t) \sim A(\bar{t}_j)$, with $\bar{t}_j$ some value between $[t_j, t_j + \tau_j]$. Then inside this interval the following is true:

$$\mathbf{y}(t_{j+1}) = e^{\tau_j \mathbf{A}_j}\mathbf{y}(t_j), \qquad \tau_j = t_{j+1} - t_j, \tag{A.32}$$

$\mathbf{A}_j \equiv \mathbf{A}(\bar{t}_j)$. Repeated evaluation of the above expression for $j = 1, 2, \dots, n_t$, formally results in

$$\mathbf{y}(t + \tau) = e^{\tau_k \mathbf{A}_k}e^{\tau_{k-1}\mathbf{A}_{k-1}} \cdots e^{\tau_1 \mathbf{A}_1}\mathbf{y}(t_0),$$

with $\tau = \sum_{j=1}^{k}\tau_j$, with $\mathbf{A}_j$, $j = 1, 2, \dots$ evaluated at times $\bar{t}_1 < \bar{t}_2 < \cdots < \bar{t}_k$. A typical choice for $\bar{t}_j$ is to take it at the middle of the time interval above, so that $\bar{t}_j = t_j + \tau_j/2$. Then the problem is to compute efficiently and accurately $e^{\tau \mathbf{A}}\mathbf{y}$.[4] A thorough review of matrix exponentiation methods in combination with practical calculations can be found in the review by Moler and Van Loan [5].

The following exponentiation of a general matrix 2×2 is often useful. Taking the matrix, $\mathbf{A}$, to be a 2×2 matrix, then the exponent can conveniently be written as

[4] *Vice versa*, the computation of a matrix exponent can be approached using algorithms that solve the corresponding ODE (A.30) with $\mathbf{A}$ constant. Nevertheless, generally solving an ODE is more costly than using other available methods of matrix exponentiation.

$$e^{t\mathbf{A}} = e^{\gamma t/2}\left[\mathbf{I}_2 \cosh\left(\frac{\tilde{D}t}{2}\right) + \frac{\tilde{\mathbf{D}}}{\tilde{D}} \sinh\left(\frac{\tilde{D}t}{2}\right)\right], \qquad \tilde{\mathbf{D}} = 2\mathbf{A} - \gamma\mathbf{I}, \tag{A.33}$$
$$\gamma = \mathrm{Tr}(\mathbf{A}), \qquad \tilde{D} = \sqrt{Det(\tilde{\mathbf{D}})}.$$

$\mathbf{I}_2$ is the 2×2 diagonal matrix and Tr() and Det() denote the *trace* and *determinant* of a square matrix, respectively.

References

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