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Technical Report

Exchange Energy for Two-Active-Electron Diatomic Systems within the Surface Integral Method

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Abstract

We have analyzed and reduced a general (quantum-mechanical) expression for the atom-atom exchange energy formulated as a five-dimensional surface integral, which arises in studying the charge exchange processes in diatomic molecules. It is shown that this five-dimensional surface integral can be decoupled into a three-dimensional integral and a two-dimensional angular integral which can be solved analytically using a special decomposition. Exact solutions of the two-dimensional angular integrals are presented and generalized. Algebraic aspects, invariance properties and exact solutions of integrals involving Legendre and Chebyshev polynomials are also discussed.

1 Introduction

In [1–3], we presented a method for obtaining the exchange energy splitting ΔE based on the Holstein-Herring method [1] for diatomic molecular systems. We started from the electronic Schrödinger wave equation in atomic units for the *one-active* electron diatomic system:

$$\left(-\frac{1}{2}\nabla^2 + V\right)\psi_\pm \;=\; E_\pm\,\psi_\pm \tag{1}$$

for the wave functions which are symmetric $(+)$ or anti-symmetric $(-)$ under exchange of the nuclei A and B. Here V is the electron-nuclear Coulomb potential energy function and E is the (electronic) energy of a given quantum mechanical state (eigenstate), with the electronic state function $\psi = \psi(\mathbf{r})$ depending on the spatial coordinates of the electron.

In previous work [3], it was shown that by multiplying the wave equation of ψ_+ on the left by ψ_- and the corresponding equation of ψ_- on the left by ψ_+, exploitation of symmetry and the divergence theorem, we could obtain the following result [3–6]:

$$\Delta E = \,-\,2\,\frac{\int_M \phi_A \boldsymbol{\nabla}\phi_A \cdot \mathrm{d}\mathbf{S}}{1 - 2\int_{right}\phi_A^2\,\mathrm{d}V} \tag{2}$$

where $\mathrm{d}\mathbf{S}$ is a differential surface element and $\int_{right}$ represents volume integration over the space on the right of the surface M. The quantity $\phi_A = (\psi_+ + \psi_-)/\sqrt{2}$ is a wave function *localized* about atom A. Eq. (2) is known as the Herring-Holstein formula.

In the previous work [2,3], we solved the one-active-electron system applicable to a diatomic atom-ion molecule where $\mathrm{d}\mathbf{S}$ in (2) is a surface element on the mid-plane between the nuclei A and B. The exchange energy ΔE vanishes exponentially with increasing internuclear distance R and therefore becomes very difficult to calculate by conventional *ab initio* methods.

Exchange effects are of prominent importance in theories of molecular binding relevant to magnetism, atmospheric physics and astrophysics. Thus, though these exchange effects are physically interesting, they are small and elusive and consequently and very difficult to calculate accurately by conventional variational methods [1, c].

In this work, we present an extension of our method to atom-atom systems. This is far more difficult as it involves *two-active electron* diatomic molecules. Two active electrons entail *electronic correlation*, which often requires delicate handling for precise calculations. The atom-atom problem is important because it has direct applications to the calculation of exchange effects in molecules such as the hydrogen molecule H_2, Li_2 and all alkali dimers M_2 isovalent to H_2.

Furthermore, since exchange operates pair-wise, a general formula for the two-active-electron case can be readily extended to the four-active electron case and allow us to calculate the exchange energies of diatomic calcium, Ca_2, which is of great importance in Bose-Einstein condensation. A combination of the formula for the one-active electron case in previous work and those presented in [2] and here provides the means to handle a wide class of diatomic systems.

We emphasize that we do not want to resort to N-dimensional integration codes or Monte-Carlo methods carelessly: from our previous experience with the one-active electron problem in computing such an elusive quantity as the exchange energy ΔE at large internuclear distances [3], we need reliable and accurate computations. In view of the difficulty of the problem and, from our previous experience, the need for precise results, we emphasize numerical as well as an algebraic analysis. In general, the results are to be calculated using a FORTRAN program generated through a link from a computer algebra program.

As shown by Herring and Flicker [1, (e)] and in this work, the surface integral for the two-electron case is five-dimensional. This can be decoupled into a three-dimensional integral and a two-dimensional angular integral, but there is the issue of decoupling the correlation terms involving the distance between the two electrons r_{12}.

This work focuses on the mathematical treatment for handling the correlation terms and should be viewed as an extension of the formula for the one-active electron case [3]. The results are tested on the ground state of H_2. The work concludes with some general observations.

2 General Formula for a Diatomic Two-Active Electron System

The electronic Schrödinger wave equation for the simplest diatomic system, the hydrogen molecule H_2 (composed of two fixed nuclear centers, labeled A and B, and two electrons), can be written as:

$$\left(-\frac{\hbar^2}{2m_\mathrm{e}}\nabla_1^2 - \frac{\hbar^2}{2m_\mathrm{e}}\nabla_2^2 + V \right) \psi = E\psi \tag{3}$$

$$\text{with} \quad V = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{12}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} \right) .$$

where the electronic state function $\psi = \psi(\mathbf{r}_1, \mathbf{r}_2)$ depends on the spatial coordinates of the electrons. An additive term $1/R$, which is constant for fixed internuclear distance R, has been omitted in the potential V, since it merely shifts all the eigenvalues. The distances between the nuclei A and B and the electron k are denoted respectively by r_{Ak} and r_{Bk}. In atomic units $\hbar = m_\mathrm{e} = e = 4\pi\varepsilon_0 = 1$.

The term $1/r_{12}$ represents the Coulomb repulsion between the two electrons and gives rise to *electronic correlation*. Its presence is what prevents the partial differential equation in (3) from being exactly separable, thus making the many-body problem intractable. In general, correlation terms are problematic and necessitate special treatment (and considerable "machinery") in quantum chemistry.

For sufficiently large internuclear distances R, the volume integration over the space to the right of M in the Holstein-Herring formula eq. (2) is exponentially sub-dominant and can therefore be neglected. Consequently, the denominator in (2) can be taken as unity; deviations from unity can be and should be calculated by the standard methods of e.g. quantum chemistry. Thus, we need only consider the surface integral in the numerator of the Holstein-Herring formula:

$$\int_M \phi_A \boldsymbol{\nabla} \phi_A \cdot \mathrm{d}\mathbf{S} \tag{4}$$

The extension to the two-active electron case is relatively straightforward. Since the two active electrons have exactly the same mass, we can formally combine the two electrons into one "object" with six rather than three spatial coordinates. Thus the Laplacians in the kinetic energy term of the Schrödinger wave equation in (3) can be combined into a single six-dimensional Laplacian. In retracing the steps from eq. (3) to eq. (13) of ref. ([3]), this requires generalizing the formula in (4) to six dimensions. Formally, this involves introducing a six-dimensional coordinate space. The resulting hypersurface as defined by Herring and Flicker [1, (e)] results from letting:

$$r_{A1}^2 + r_{B2}^2 = r_{B1}^2 + r_{A2}^2$$

or equivalently:

$$z_1 = z_2$$

The end result is a five-dimensional hypersurface. As derived in the work of [7], the surface integral as expressed in (4) can be written as [8, (1)]:

$$\begin{aligned} I \;=\; & \int_{-1}^{1} \mathrm{d}\zeta \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \mathrm{d}x_1\,\mathrm{d}x_2\,\mathrm{d}y_1\,\mathrm{d}y_2 \\ & \left[{\Psi'}_{II}^{*}(2,1)\frac{\partial \Psi_I(1,2)}{\partial z'} - \Psi_I^*(1,2)\frac{\partial {\Psi'}_{II}(2,1)}{\partial z'} \right]_{z'=0} \end{aligned} \tag{5}$$

where $\{x_i, y_i, z_i\}$, $i = 1$ and 2, are the electronic Cartesian coordinates and:

$$z = \frac{1}{2}(z_1 + z_2) = \zeta\,\frac{R}{2} \quad \text{and} \quad z' = (z_1 - z_2) \tag{6}$$

The quantity ζ is a dimensionless variable whose usefulness will become clearer when we need to differentiate the resulting integral with respect to R. The integration over the (x_i, y_i) coordinates is over all space as shown by Herring and Flicker [1, V,(e)] and the integration over the final coordinate $z = z_1 = z_2$ is only over the region $-\frac{R}{2} < z < \frac{R}{2}$ (or equivalently $-1 < \zeta < 1$), since integration outside this region contributes only exponentially sub-dominant terms.

In the general case of *two-active-electron* systems, such as diatomic alkali dimers M_2, isovalent to H_2, the wave functions are constructed as linear combinations of Slater-type functions ϕ in complete analogy to the atom-ion case [2]. They are corrected by a polarization term $\chi(\mathbf{r}_1, \mathbf{r}_2)$.

$$\begin{aligned} \Psi_I(1,2) &= \sum_{A\,B} \phi_A(1)\,\phi_B(2)\,\chi_I(1,2) \\ & \quad P_{\ell_A}^{m_A}(\cos\theta_1) P_{\ell_B}^{m_B}(\cos\theta_2)\;\exp(\mathrm{i}(m_A\,\phi_1 + m_B\,\phi_2))\,, \\ {\Psi'}_{II}(2,1) &= \sum_{A'\,B'} {\phi'}_{A'}(2)\,{\phi'}_{B'}(1)\,{\chi'}_{II}(2,1) \\ & \quad P_{{\ell'}_{B'}}^{{m'}_{B'}}(\cos{\theta'}_1) P_{{\ell'}_{A'}}^{{m'}_{A'}}(\cos{\theta'}_2)\;\exp(\mathrm{i}({m'}_{A'}\,{\phi'}_2 + {m'}_{B'}\,{\phi'}_1))\,. \end{aligned} \tag{7}$$

where $\{\ell_A, m_A\}$, $\{\ell_B, m_B\}$ and their primed counterparts are atomic angular quantum numbers, and

$$\begin{aligned} \phi_A(1) &= \mathcal{A}_A\, r_1^{\gamma_A}\;\exp(-\alpha_A\, r_1) \\ \phi_B(2) &= \mathcal{B}_B\, r_2^{\delta_B}\;\exp(-\beta_B\, r_2) \\ {\phi'}_{A'}(2) &= {\mathcal{A}'}_{A'}\, {r'}_2^{{\gamma'}_{A'}}\;\exp(-{\alpha'}_{A'}\;{r'}_2) \\ {\phi'}_{B'}(1) &= {\mathcal{B}'}_{B'}\, {r'}_1^{{\delta'}_{B'}}\;\exp(-{\beta'}_{B'}\;{r'}_1) \end{aligned} \tag{8}$$

where $\{\mathcal{A}_A, \mathcal{B}_B, \gamma_A, \delta_B, \alpha_A, \beta_B\}$ and their primed counterparts are known parameters characterizing the radial part of the atomic wave functions. They can be deduced from the solution of the *one-active-electron* Schrödinger wave equation for the atom under consideration. Just as in the one-active electron case [3], these parameters are identified from atomic wave functions and physical-chemical considerations. The polarization functions χ are given by Smirnov and Chibisov [10]. In the case when $z_1 = z_2 = z$, these functions are, for $z > 0$

$$\begin{aligned}
\chi_I(1,2) &= \left(\frac{1}{2}\right)^{1/\beta_B} (\beta_B)^{-\beta_B/\alpha_A\mu_{AB}} \, (\mu_{AB})^{1/\alpha_A} (\rho_{12})^{1/\mu_{AB}} \\
&\quad \times (\zeta+1)^{-1/\beta_B} \exp\left[-\frac{1}{2\,\beta_B}(1-\zeta)\right] \\
&\quad \times \left\{ \left[\mu_{AB}^2 (\tfrac{R}{2}(1-\zeta))^2 + (\beta_B \rho_{12})^2\right]^{1/2} + \mu_{AB}(\tfrac{R}{2}(1-\zeta)) \right\}^{-1/\mu_{AB}} \\
\chi_{II}(2,1) &= \chi_I(1,2)
\end{aligned} \tag{9}$$

and for $z < 0$

$$\begin{aligned}
\chi_I(1,2) &= \left(\frac{1}{2}\right)^{1/\alpha_A} (\alpha_A)^{-\alpha_A/\beta_B\mu_{AB}} \, (\mu_{AB})^{1/\beta_B} (\rho_{12})^{1/\mu_{AB}} \\
&\quad \times (1-\zeta)^{-1/\alpha_A} \exp\left[-\frac{1}{2\,\alpha_B}(1+\zeta)\right] \\
&\quad \times \left\{ \left[\mu_{AB}^2 (\tfrac{R}{2}(1+\zeta))^2 + (\alpha_A \rho_{12})^2\right]^{1/2} + \mu_{AB}(\tfrac{R}{2}(1+\zeta)) \right\}^{-1/\mu_{AB}} \\
\chi_{II}(2,1) &= \chi_I(1,2)
\end{aligned} \tag{10}$$

where

$$\begin{aligned}
\mu_{AB} &= \alpha_A + \beta_B \\
\rho_{12}^2 &= (x_1 - x_2)^2 + (y_1 - y_2)^2
\end{aligned} \tag{11}$$

Note that the expression for $\chi_I(1,2)$ for $z < 0$ can be obtained from that for $z > 0$ simply by replacing z with $-z$ and by exchanging these parameters:

$$\alpha_A \leftrightarrow \beta_B$$

By inserting the wave functions of (7) with the polarization corrections of (9) and (10) into the surface integral of (5), we finally get:

$$\begin{aligned}
I &= \sum_{A\ B\ A'\ B'} \mathcal{A}_A \, \mathcal{B}_B \, \mathcal{A}'{}_{A'} \, \mathcal{B}'{}_{B'} \\
&\times \ \{ \sum_{k_i=0} \mathcal{P}_{k_1}^{(\ell_A, m_A)} \, \mathcal{P}_{k_2}^{(\ell_B, m_B)} \, \mathcal{P}_{k_3}^{(\ell'{}_{B'}, m'{}_{B'})} \mathcal{P}_{k_4}^{(\ell'{}_{A'}, m'{}_{A'})} \} \\
&\times \ \left\{ \int_{-1}^{1} \mathrm{d}\zeta \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}x_1 \, \mathrm{d}x_2 \, \mathrm{d}y_1 \, \mathrm{d}y_2 \, \frac{\partial Q(\zeta, R)}{\partial R} \right\}
\end{aligned} \tag{12}$$

where $\mathcal{P}_k^{(\ell,m)}$ are coefficients in the decomposition of the associated Legendre functions [13] according to:

$$P_\ell^m(\cos\theta) = \sum_{k}^{\ell-m} \mathcal{P}_k^{(\ell,m)} \cos^k\theta \, \sin^m\theta \tag{13}$$

and

$$
\begin{aligned}
Q(\zeta,R) &= \left(\tfrac{R}{2}\right)^{k_1+k_2+k_3+k_4+1} (\zeta+1)^{k_1+k_4}\,(\zeta-1)^{k_2+k_3}\;\rho_1^{2\,M_1}\rho_2^{2\,M_2}\\
&\times\; \chi_I(1,2)\chi'_{II}(2,1)\\
&\times\; \left(\rho_1^2+(\tfrac{R}{2}(\zeta+1))^2\right)^{\tau_1/2}\left(\rho_2^2+(\tfrac{R}{2}(\zeta-1))^2\right)^{\tau_2/2}\\
&\times\; \left(\rho_2^2+(\tfrac{R}{2}(\zeta+1))^2\right)^{\tau_4/2}\left(\rho_1^2+(\tfrac{R}{2}(\zeta-1))^2\right)^{\tau_3/2}\\
&\times\; \cos[(m_A-m'_{B'})\,(\phi_1-\phi_2)]\\
&\times\; \exp\left[-\alpha_A\,(\rho_1^2+(\tfrac{R}{2}\,(\zeta+1))^2)^{1/2}-\beta'_{B'}\,(\rho_1^2+(\tfrac{R}{2}\,(\zeta-1))^2)^{1/2}\right]\\
&\times\; \exp\left[-\alpha'_{A'}\,(\rho_2^2+(\tfrac{R}{2}\,(\zeta+1))^2)^{1/2}-\beta_B\,(\rho_2^2+(\tfrac{R}{2}\,(\zeta-1))^2)^{1/2}\right]
\end{aligned}
\tag{14}
$$

and

$$
\begin{aligned}
\tau_1 &= \gamma_A-k_1-m_A & \tau_2 &= \delta_B-k_2-m_B\\
\tau_4 &= \gamma'_{A'}-k_4-m'_{A'} & \tau_3 &= \delta'_{B'}-k_3-m'_{B'}\\
2M_1 &= m_A+m'_{B'} & 2M_2 &= m'_{A'}+m_B\,.
\end{aligned}
\tag{15}
$$

Note that $m_A+m'_{B'}$ and $m'_{A'}+m_B$ are even integers, which ensures that M_1 and M_2 defined above are integers.

3 Method of Solution

In either the general case of eq. (12), or when all angular quantum numbers ℓ and m are zero, one has to deal with a very challenging five-dimensional surface integral.

3.1 Symbolic and Numerical Analysis

It is well known that integration over the Cartesian coordinates (x_i, y_i) where $i=1,2$ can be readily transformed into integrals over cylindrical coordinates as follows:

$$
\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}x_i\,\mathrm{d}y_i \quad\to\quad \int_0^{\infty}\mathrm{d}\rho_i\rho_i\int_0^{2\pi}\mathrm{d}\phi_i
$$

We note that most terms in the surface integral (12) depend on the (scalar) radial coordinates ρ_1 and ρ_2. The term $\cos[(m_A-m'_{B'})\,(\phi_1-\phi_2)]$ reduces to unity if $m_A=m'_{B'}$ (a large number of cases), is multiplicative and consequently separable from the radial integrals. We also note that the $\mathcal{P}_k^{(\ell,m)}$ are coefficients of the associated Legendre functions according to eq. (13). Thus the five-dimensional integral could be exactly decoupled if it were not for the correlation term ρ_{12} which appears in the polarization corrections of eqs. (9) and (10).

For the sake of accuracy and economy of computation (both symbolic and numeric), it is highly desirable to deal with functions of the correlation term ρ_{12}. This becomes acute when we apply numerical analysis to the integrals. Consider an integral of the form:

$$
\int_0^{\infty}\mathrm{d}\rho_i\;f_i(\rho_i)\;\exp\left(-c_1\sqrt{\rho_i^2+(\tfrac{R}{2}(\zeta+1))^2}-c_2\sqrt{\rho_i^2+(\tfrac{R}{2}(\zeta-1))^2}\right)
\tag{16}
$$

where f_i is an algebraic function and $i=1,2$ corresponds to one of the integrations over ρ_1 or ρ_2 . We make the variable transformations:

$$
X_i^2 \;=\; \left(\tfrac{R}{2}(\zeta+1)\right)^2\;+\;\rho_i^2.
\tag{17}
$$

For $0 \leq z \leq \frac{R}{2}$ (or equivalently $0 \leq \zeta \leq 1$), we obtain an integral of the form:

$$\int_{z+\frac{R}{2}}^{\infty} \mathrm{d}X_i \; g_i(X_i) \; \exp\left(- c_1 \, X_i \; - \; c_2\sqrt{X_i^2 \; - \; \zeta R^2} \right) \tag{18}$$

where g_i is an algebraic function. If we let:

$$u_i \;=\; - \; c_1 \, X_i \; - \; c_2 \, \sqrt{X_i^2 \; - \; \zeta R^2} \, , \tag{19}$$

this imposes the quadratic condition:

$$- \, 2 \, u_i \, c_2 X_i \; + \; (u_i^2 \; + \; \zeta \, c_2^2 \, R^2) \; = \; 0 \, . \tag{20}$$

For simplicity, we consider the case when $c \; = \; c_1 \; = \; c_2$, and thus

$$X_i \;=\; \frac{u_i}{2\,c} \;+\; \frac{\zeta \, R^2 \, c}{2 \, u_i} \qquad (c = c_1 = c_2) \, . \tag{21}$$

The lower endpoint u_o is given by:

$$u_o = c\tfrac{R}{2}(\zeta+1)) \left[1 + \sqrt{1 - \frac{4\zeta}{(\zeta+1)^2}} \, \right] \;=\; c\, R \, , \qquad 0 \leq \zeta \leq 1$$

Although the analysis was done for the simple case $c_1 = c_2$, for $c_1 \neq c_2$, one can always return to the roots of (19). Thus the twice transformed integral of (18) has the simple and recognizable form:

$$\int_{c\,R}^{\infty} \mathrm{d}u_i \; e^{-u_i} \; h_i(u_i) \tag{22}$$

where h_i is algebraic. This result is very instructive. From our experience and in analogy to the one-active electron case [2, 4], we can see that the numerical integrations over ρ_i where $i = 1, 2$ can be performed accurately by normalized (scaled) Gauss-Laguerre quadrature, namely [13, 25.4.45]. We can also see that final integration over z of the surface integral in (12) can also be readily obtained from Gauss-Legendre quadrature using [13, 25.4.29]. Everything can be reduced to a three-dimensional integral which can be accurately calculated via three nested quadratures provided, of course, that the remaining angular integrations over ϕ_1 and ϕ_2 are addressed.

The function $Q(\zeta, R)$ in the surface integral (12) involves the product $U \;=\; \chi_I(1,2){\chi'}_{II}(2,1)$. Smirnov and Chibisov have considered the case where ρ_{12} is negligible compared to R. We can consider formal expansions of this product, and its derivatives with respect to R, which are required in (12), with respect to $Y \;=\; \frac{R}{2}(1 \pm \zeta)$. Thus we can consider three regimes and their associated functional forms:

$$\rho_{12} \; < \; Y \quad \rightarrow \quad U \; \approx \; U_0 \, \rho_{12}^{p} \; + \; U_1 \, \frac{\rho_{12}^{p+2}}{Y^2} \; + \; U_2 \, \frac{\rho_{12}^{p+4}}{Y^4} \cdots \tag{23}$$

$$\rho_{12} \; > \; Y \quad \rightarrow \quad U \; \approx \; Q_0 \, \rho_{12}^{q} \; + \; Q_1 \, Y^2 \, \rho_{12}^{q-2} \; + \; Q_2 \, Y^4 \, \rho_{12}^{q-4} \cdots \tag{24}$$

$$\rho_{12} \; \approx \; Y \quad \rightarrow \quad U \; \approx \; \rho_{12}^{w} \left(W_0 \; + \; W_1 \, (\rho_{12} - Y) \; + \; W_2 \, (\rho_{12} - Y)^2 \ldots \right)$$

The expansions can be worked out to high order using a computer algebra system and the resulting coefficients stored for computation in FORTRAN using Macrofort [14]. In each of these regimes, we have to deal with an angular average of the form:

$$\int_0^{2\pi} \int_0^{2\pi} \mathrm{d}\phi_1 \; \mathrm{d}\phi_2 \; \rho_{12}^{\nu} \tag{25}$$

where ν is a real number.

3.2 Decomposition of Correlation terms

Correlation terms of the form ρ_{12}^n can be expanded as follows (see [11, eq. (19)] and [12, 5.17.5]):

$$\rho_{12}^n \;=\; |\rho_1 - \rho_2|^n \;=\; \sum_k a_k^n(\rho_<, \rho_>)\, P_k(\cos\omega) \tag{26}$$

where ω is the angle between the two vectors ρ_1 and ρ_2 and $\rho_< \;=\; \min(\rho_1, \rho_2)$ and $\rho_> \;=\; \max(\rho_1, \rho_2)$. In the two-dimensional plane considered here $(z_1 = z_2 = 0)$, the magnitude of this angle is simply $\omega = \phi_1 - \phi_2$. The coefficients a_k^n of this decomposition are given by:

$$a_k^n(\rho_<, \rho_>) \;=\; \frac{\left(-\frac{n}{2}\right)_k}{\left(\frac{1}{2}\right)_k}\, \rho_>^n \left(\frac{\rho_<}{\rho_>}\right)^k {}_2F_1\left(k - \frac{n}{2}, -\frac{1}{2} - \frac{n}{2}; k + \frac{3}{2}; \frac{\rho_<^2}{\rho_>^2}\right),$$

where ${}_2F_1(a, b; c; z)$ is the Gauss hypergeometric function [13]. The above is [12, 5.17.5]. There are also equivalent formulae symmetric in ρ_1 and ρ_2 such as [11, eq. (27b)] and [12, eq. (32)]:

$$a_k^n(\rho_<, \rho_>) \;=\; \frac{\left(-\frac{n}{2}\right)_k}{\left(\frac{1}{2}\right)_k}\, \frac{(\rho_1\rho_2)^k}{(\rho_1 + \rho_2)^{2k-n}}\, {}_2F_1\left(k - \frac{n}{2}, k + 1; 2k + 2; \frac{4\rho_1\rho_2}{(\rho_1 + \rho_2)^2}\right).$$

Varshalovich *et al.* assume that n is an integer. However, it is found that this decomposition holds not only for integer n but more generally for any $n = \nu$ real! This can be verified by examining the details of the derivation of these formulae. At any rate, this can be readily demonstrated by plugging in specific values and verifying the numbers with a computer algebra system. The realization that $n = \nu$ can have any real value is vital to this analysis.

3.3 Angular Integration

It appears that we are faced with evaluating the integral:

$$\int_0^{2\pi}\int_0^{2\pi} \mathrm{d}\phi_2\, \mathrm{d}\phi_1\; P_k(\cos\omega)\cos(m\,\omega) \tag{27}$$

where $\omega = \phi_1 - \phi_2$ and for which there is no expression in the literature.

Special case $m = 0$

We use the explicit expansion of the Legendre polynomials in eq. (57) of the appendix. Thus, one has to consider integrals of the form:

$$\int_0^{2\pi} \mathrm{d}\phi_1\, \cos^i\omega \tag{28}$$

Exact solutions divide into even and odd i cases and can be obtained from $(1.5.3.3)$ and $(1.5.3.5)$ of Prudnikov *et al.* [18]:

$$\begin{aligned}
\int \mathrm{d}t\cos^{2j}t \;&=\; \frac{1}{2^{2j}}\binom{2j}{j}\, t \;+\; \frac{1}{2^{2j-1}}\sum_{k=0}^{j-1}\binom{2j}{k}\frac{\sin(2j-2k)t}{2j-2k}\\
\int \mathrm{d}t\cos^{2j+1}t \;&=\; \frac{1}{2^{2j}}\sum_{k=0}^{j}\binom{2j+1}{k}\frac{\sin(2j-2k+1)t}{2j-2k+1}
\end{aligned} \tag{29}$$

where $j = 0, 1, 2\ldots$ It is worthwhile examining these in detail: when the endpoints are plugged in, everything except for the very first term on the right of $(1.5.3.3)$ cancels out. Thus, only the even terms $i = 2j$ contribute:

$$\int_0^{2\pi} \mathrm{d}\phi_1 \cos^{2j}\omega \;=\; \frac{2\pi}{2^{2j}} \left(\begin{array}{c} 2j \\ j \end{array} \right) \tag{30}$$

where $\omega = \phi_1 - \phi_2$. Here the variable ϕ_2 does not appear on the right side of (30). Thus, the inner integral (28) is *independent* of ϕ_2. Because of this invariance, the outer integration trivially reduces to simple multiplication of the right side by 2π. By combining (30) and (57) and after a series of manipulations and simplifications, it is found that:

$$\begin{aligned} \int_0^{2\pi} \int_0^{2\pi} \mathrm{d}\phi_2\, \mathrm{d}\phi_1\; P_{2j}(\cos\omega) &= f_j \\ \int_0^{2\pi} \int_0^{2\pi} \mathrm{d}\phi_2\, \mathrm{d}\phi_1\; P_{2j+1}(\cos\omega) &= 0\,. \end{aligned} \tag{31}$$

where $j = 0, 1, 2, \ldots$ and

$$f_j \;=\; 4\pi^2 \left[\frac{(2j-1)!!}{(2j)!!} \right]^2$$

which is equivalently defined by the recursion formula:

$$\begin{aligned} f_0 &= 4\pi^2 \\ f_j &= \left(\frac{2j-1}{2j} \right)^2 f_{j-1} \quad j > 0 \quad j = 1, 2, \ldots \end{aligned} \tag{32}$$

which is very amenable to computation and where $n!!$ denotes the double factorial of n (see appendix). The results above have been verified numerically using computer algebra.

Armed with the realization that these particular integrals are invariant with respect to ϕ_2, we can now obtain the solution by setting $\phi_2 = 0$, since the value of ϕ_2 does not affect the final result:

$$\int_0^{2\pi} \mathrm{d}\phi_1\, P_{2j}(\cos\phi_1) \;=\; 2 \int_{-1}^{1} \mathrm{d}y\, \frac{P_{2j}(y)}{\sqrt{1-y^2}} \;=\; 2\pi \left[\frac{(2j-1)!!}{(2j)!!} \right]^2 \tag{33}$$

which is a well known result in view of [20, 7.226.1] and $(21:10:5)$ of [22, p.169].

General Case

The invariance property is clearly valid, not only for the general class of integrals in (27), but also for the more general class:

$$\int_0^{2\pi} \int_0^{2\pi} \mathrm{d}\phi_2\, \mathrm{d}\phi_1\; P_k(\cos\omega) \cos(m\,\omega) f^i(\omega) \tag{34}$$

where $f = \cos$ or $\sin$ (or a product of trigonometric functions), as shown in the appendix. This invariance allows us to decouple the angular integrations and reduces the complexity of the computations by an order of magnitude. The expressions for all the angular integrals have closed forms in terms of fractions. These can obtained directly or from recursion formulae as shown in the appendix.

The inclusion of a factor $\cos^i\omega$ into the integral (27) is important because it allows us to exploit the following recursion procedure:

$$\begin{aligned} \rho_{12}^{n+2} &= \rho_{12}^{n}\, \rho_{12}^{2} \\ &= \rho_{12}^{n} \left(\rho_1^2 \,+\, \rho_2^2 \,-\, 2\,\rho_1\,\rho_2 \cos\omega \right) \end{aligned}$$

and thus the double angular integration denoted $< \; >_\omega$ yields:

$$< \rho_{12}^{n+2} >_\omega \;=\; (\rho_1^2 \,+\, \rho_2^2) \;< \rho_{12}^{n} >_\omega \;-\; 2\,\rho_1\,\rho_2 \;< \rho_{12}^{n} \cos\omega >_\omega \;. \tag{35}$$

Thus for a given $< \rho_{12}^n >_\omega$, we can readily calculate $< \rho_{12}^{n+2} >_\omega$, $< \rho_{12}^{n+4} >_\omega$, etc. in the series expansion for small ρ_{12} in (23). This is important for the following reasons. The hypergeometric coefficients in the expansion for ρ_{12}^n can be readily calculated from Robert Forrey's program [23], but this is more "expensive" than by using the rational expressions for the double integrated angular components.

Thus for the same effort in computing the hypergeometric coefficients for any given $< \rho_{12}^n >_\omega$, we can also compute $< \rho_{12}^n >_\omega \;\; \cos^i(\omega)$ to obtain $< \rho_{12}^{n+i} >_\omega$ where $i = 1, 2, \ldots$ for the series expansion in small ρ_{12}^n of the polarization terms. This is made all the more feasible by using the optimizer for finding common sub-expressions in computer algebra. In the case of large ρ_{12}, it is found that the resulting series requires only integer inverse powers of ρ_{12}, namely ρ_{12}^{-i} where $i = 1, 2, \ldots$, allowing the possibility of more rapid computation by simplification of the hypergeometric coefficients.

Moreover, since the invariance property holds for any $< \rho_{12}^n >_\omega$, where n is a real number, it follows that the same property should hold for the product $U = \chi_I(1,2)\chi'_{II}(2,1)$ *before* any series expansions. This has been checked numerically. This allows one to set $\phi_2 = 0$ in the direct numerical integration of this product over ϕ_1 using a Gauss-Legendre procedure and multiply the result by 2π to obtain the final integrated result over ϕ_2. This is a feasible alternative for the mid-range when ρ_{12} is neither very large nor very small in relation to $Y = \frac{R}{2}(1 \pm \zeta)$ and provides a numerical check for the double angular integration of the series expansions in (23) and (24).

4 Results

4.1 Herring and Flicker (revisited)

The hydrogen molecule H_2 provides a good test because we know closed-form eigensolutions for the hydrogen atom. Also it is illustrative for other atom-atom systems. We consider the ground state where $\ell_i = m_i = 0$ and thus a special case of (12) is applicable. Taking eq. (18) for $J = \frac{1}{2}(E_+ - E_-)$ from Herring and Flicker [1, (e)][1]

$$\begin{aligned} J \;&\approx\; \frac{8R^3}{\pi^2} e^{-1-2R} \int_{-1}^{1} \mathrm{d}\zeta \int\!\!\int\!\!\int\!\!\int \mathrm{d}x_1\,\mathrm{d}y_1\,\mathrm{d}x_2\,\mathrm{d}y_2 \\ &\quad \times \exp\left[-\frac{2\,(\rho_1^2+\rho_2^2)}{R\,(1-\zeta^2)} + |\zeta| \right] \\ &\quad \times \frac{\rho_{12}}{R^3\,(1\,+\,|\zeta|)^2\,(1\,-\,|\zeta|)} \end{aligned} \tag{36}$$

which has been written in terms of the dimensionless variable ζ, where $z = \frac{R}{2}\zeta$ and where it is understood that integration over the Cartesian coordinates (x_i, y_i) is exactly as in our own formula (12). After decoupling the correlation term ρ_{12} in terms of ρ_i where $i = 1, 2$ and transforming to cylindrical coordinates (as discussed in section 3), we find that the resulting integrals in ρ_i are exactly solvable [19] and implemented in various computer algebra systems.

---

[1] To account for eq. (19) of their work [1, (e)], we must assume there is a mistake in sign in front of the term $2|z|/R$ in eq. (18).

For the integration in z, we make the transformation $q = 1 - (2|z|/R)$ (or equivalently $q = 1 - |\zeta|$) to obtain:

$$J \;=\; C\,R^{5/2}e^{-2R} \int_0^1 \mathrm{d}q\; e^{-q}q^{3/2}(2-q)^{1/2} \tag{37}$$

An exact expression for the integral in (37) can be obtained from (3.385) of [20] (with parameters: $\lambda = 1\ ,\ \beta = \frac{1}{2}\ ,\ \rho = -\frac{1}{2}\ ,\ \mu = 1\ ,\ \nu = \frac{5}{2}$). Thus,

$$\int_0^1 \mathrm{d}q\; e^{-q}q^{3/2}(2-q)^{1/2} \;=\; \sqrt{2}\,B\left(\frac{5}{2},1\right)\;\Phi_1\left(\frac{5}{2},-\frac{1}{2},\frac{7}{2};\frac{1}{2},-1\right) \tag{38}$$

where $B(a,b)$ is Euler's beta function and Φ_1 is a degenerate hypergeometric function [20] (confluent function of two variables). Eq. (38) can be further reduced to the much simpler expression

$$\int_0^1 dq\; e^{-q}q^{3/2}(2-q)^{1/2} = \tag{39}$$

$$\frac{\pi}{4e}[4I_1(1) + 4\mathbf{L}_1(1) - I_0(1) - I_2(1) - \mathbf{L}_0(1) - \mathbf{L}_2(1)] - \frac{1}{6e},$$

where $I_n(z)$ is the modified Bessel function and $\mathbf{L}_n(z)$ is the Struve function which are available in most symbolic computer packages and standard references (e.g. see [13]). According to eq. (19) of Herring and Flicker [1, (e)], the constant $C \;=\; C_{HF}$ is given by:

$$C_{HF} \;=\; -\,2\pi^{1/2} \quad\Rightarrow\quad J \;=\; -\,0.818\,R^{5/2}e^{-2R}. \tag{40}$$

This result has been verified by very accurate *ab initio* calculations and found to be valid down to $R \;=\; 6$ a.u. [21].

We also get the result in (37), but the value of C varies depending on how many terms we use in the series expansion in (26) for the radial separation ρ_{12}. To this end, we multiplied the coefficient a_k^n in (26) by λ^k, where λ acts as an ordering parameter, and we computed the ratio C_λ/C_{HF} as a series in powers of λ:

$$\begin{aligned}\frac{C_\lambda}{C_{HF}} \;&=\; \frac{5}{3}\sqrt{2} - \frac{4}{3} + \left(\frac{13}{21} - \frac{19}{42}\sqrt{2}\right)\lambda \;+\; \left(\frac{225}{616}\sqrt{2} - \frac{639}{1232}\right)\lambda^2 \\ &+\; \left(\frac{307}{704} - \frac{163}{528}\sqrt{2}\right)\lambda^3 \;+\; \left(\frac{1981}{7296}\sqrt{2} - \frac{29897}{77824}\right)\lambda^4 \\ &+\; \left(\frac{2479869}{7159808} - \frac{27405}{111872}\sqrt{2}\right)\lambda^5 \;+\; \ldots\end{aligned} \tag{41}$$

If the decomposition in (26) converges, we expect this infinite series to converge to unity at $\lambda = 1$. This convergence is demonstrated in table 1. Upon examination of this table, what is striking is that the first term $(N = 0)$ already provides about 98% of the result and by the next term, 99.8%. The sum of the first terms converges rapidly but after $N = 2$, the convergence becomes slower.

The convergence can be accelerated by using the Levin transformations as in the previous work [3]. (e.g. see [15–17] for more details). The result from the Levin-u transformation at $N \;=\; 20$ gives unity within 18 digits. Thus, we can be confident that (41) is indeed unity at $\lambda = 1$.

What is instructive about this exercise is that it shows that only the leading term of the expansion of ρ_{12} in (26) is sufficient to get the correct asymptotic behavior of the exchange energy. Moreover, only a few terms of the decomposition in (26) are needed to obtain a sufficiently accurate calculation.

N	Partial sum	Partial sum (float)	Levin u
0	$\frac{5}{3}\sqrt{2}-\frac{4}{3}$	1.0236892706218250813361479	1.0236892706218250813361479
1	$\frac{17}{14}\sqrt{2}-\frac{5}{7}$	1.0029736114530439878306220	1.0037794141748116112912448
2	$\frac{139}{88}\sqrt{2}-\frac{217}{176}$	1.0008600587484114975390311	1.0002574346444371999261134
3	$\frac{61}{48}\sqrt{2}-\frac{51}{64}$	1.0003547355158082911854794	1.0000076148632118924726109
4	$\frac{3751}{2432}\sqrt{2}-\frac{91913}{77824}$	1.0001783809463320427858283	1.0000003402760015043278677
5	$\frac{7639}{5888}\sqrt{2}-\frac{314533}{376832}$	1.0001017795462080634843920	0.9999999733035426459251712
$\vdots$	$\vdots$	$\vdots$	$\vdots$
9		1.0000212508770144578012961	1.0000000000630044695406100
10		1.0000158826508702787415879	1.0000000000064516415368403
11		1.0000121789747699379219631	0.9999999999991189486771618
$\vdots$	$\vdots$	$\vdots$	$\vdots$
18		1.0000030097896301749543801	0.9999999999999999891042844
19		1.0000025760575289647006875	0.9999999999999999993359865
20		1.0000022217902822103715321	1.0000000000000000002397473

Table 1: Convergence of Series Expansion (41) (HF calculation)

4.2 General Asymptotic Expansions

We follow the methods of Umanskii and Voronin [9] and consider expansions of the exponential terms in $Q(\zeta, R)$ in eqs. (14) of the form:

$$\begin{aligned}
\exp\left[-\alpha_A\left(\rho_1^2+(\tfrac{R}{2}(\zeta+1))^2\right)^{1/2}\right] &= \exp\left[-\alpha_A\tfrac{R}{2}(\zeta+1)-\frac{\alpha_A\,\rho_1^2}{R(\zeta+1)}\right] \\
\exp\left[-\beta'_{B'}\left(\rho_1^2+(\tfrac{R}{2}(\zeta-1))^2\right)^{1/2}\right] &= \exp\left[-\beta'_{B'}\tfrac{R}{2}(1-\zeta)-\frac{\beta'_{B'}\,\rho_1^2}{R(1-\zeta)}\right] \\
\exp\left[-\beta_B\left(\rho_2^2+(\tfrac{R}{2}(\zeta-1))^2\right)^{1/2}\right] &= \exp\left[-\beta_B\tfrac{R}{2}(1-\zeta)-\frac{\beta_B\,\rho_2^2}{R(1-\zeta)}\right] \\
\exp\left[-\alpha'_{A'}\left(\rho_2^2+(\tfrac{R}{2}(\zeta+1))^2\right)^{1/2}\right] &= \exp\left[-\alpha'_{A'}\tfrac{R}{2}(\zeta+1)-\frac{\alpha'_{A'}\,\rho_2^2}{R(\zeta+1)}\right]
\end{aligned} \tag{42}$$

and similarly for the other terms in the surface integrals of eq. (14). Note that the expansions of Umanskii and Voronin [9] imply $\rho_i < (R/2 \pm z)$ for $i = 1, 2$. Also note that these expansions yield integrals for (12) of the form already encountered in Herring and Flicker, namely (37).

We must also note that these expansions, though yielding the leading asymptotic behavior, become uncertain beyond the first term. Moreover, we will limit ourselves only to this term because polarization corrections, as for the Herring function [1, (c)], the function of Chibisov (see [2, 3]) in the one-active electron case, and the polarization functions of (9) and (10) can only yield the correct *physical* leading term. In other words, the higher-order terms, though mathematically instructive, are not physically meaningful. Thus, we can neglect them for now; having obtained a counterpart of the Herring and Flicker formula for excited states of the hydrogen molecule is itself a considerable achievement.

Returning to the H_2 case, the wavefunctions in eqs. (7) can be written in the generic form:

$$\phi_{n,\ell,m} \;=\; \sum_{k=1}^{k_f} \mathcal{A}_k \, r^{\gamma_k} \, e^{-\alpha_k \, r} \tag{43}$$

It is well known that the Slater basis set expansions truncate to simple closed form solutions in the case of hydrogen; consequently k_f is a small number. The ground state $1s$ of the hydrogen atom has the quantum numbers $n = 1$, $\ell = 0$, $m = 0$ and the eigensolution is

$$\phi_{1,0,0} \;=\; 2e^{-r} \tag{44}$$

In matching this to eq. (43), the parameters here are obviously $k_f \;=\; 1$ and:

$$\begin{array}{llll}
\ell_A \;=\; m_A \;=\; 0 & \mathcal{A}_A \;=\; 2\,, & \gamma_A \;=\; 0\,, & \alpha_A \;=\; 1 \\
\ell_B \;=\; m_B \;=\; 0 & \mathcal{B}_B \;=\; 2\,, & \delta_B \;=\; 0\,, & \beta_B \;=\; 1 \\
\ell'_{A'} \;=\; m'_{A'} \;=\; 0 & \mathcal{A}'_{A'} \;=\; 2\,, & \gamma'_{A'} \;=\; 0\,, & \alpha'_{A'} \;=\; 1 \\
\ell'_{B'} \;=\; m'_{B'} \;=\; 0 & \mathcal{B}'_{B'} \;=\; 2\,, & \delta'_{B'} \;=\; 0\,, & \beta'_{B'} \;=\; 1
\end{array}$$

When we input these values, we obtain exactly the ground state result of H_2 shown previously. Obtaining this result required making use of a relatively small computer algebra program similar to that used for the Herring-Flicker surface integral in (37).

In the same way, we can use our general formula to yield the correct leading asymptotic behavior for the exchange energies for *excited* states of hydrogen as reported elsewhere, and also for the ground and excited states of other systems.

5 Conclusions and Comments

We have developed and analyzed a general (quantum-mechanical) formula for the exchange energy in diatomic systems which is suitable for obtaining analytic results and for numerical calculations. Analytically, the methods presented in this work allow us to get the leading asymptotic terms for any pair of symmetric and anti-symmetric states in *any* given diatomic molecular system.

An important dividend of this work is found when using cylindrical coordinates in integrating over the five-dimensional hypersurface arising in the Herring-Flicker theory. Here one has an invariance property which greatly simplifies the successive angular integrations. This invariance not only allows us to eliminate one level of integration; it also allows us to evaluate exactly the general class of double angular integrals associated with correlation terms of the form ρ_{12}^{ν} where ν is any real number. The solutions are in terms of simple fractions obtainable directly or by recursion relations. Our simple results for this five-dimensional hypersurface integration may be instructive in dealing with similar problems in quantum chemistry.

In the one-active electron case [2], we were able to get an explicit form for the leading term of the asymptotic expansions. In principle, this should apply to the two-active electron as well. In practice, however, obtaining these terms for the two-active electron case requires extensive computer algebra for any set of symmetric and anti-symmetric states. We anticipate that these programs can be generalized to larger sets of quantum states.

The leading asymptotic behavior has been obtained for the ground state of the hydrogen molecule, reproducing the Herring and Flicker result [1, (e)]. Moreover, as reported elsewhere [7], the same methods have been used to obtain the leading terms for a few excited states.

Just as in the previous one-active electron case, we have avoided "brute-force" techniques and presented solutions which are "natural" in that they come out of the mathematical properties of the quantities we analyzed. In view of the elusive nature of the quantities to be calculated, i.e. that the exchange energy is an exponentially vanishing function of R, this is even more essential in the two-active electron case which requires the solution of a five-dimensional integral.

The computer algebra and FORTRAN codes developed here can be used with confidence within a variety of physical/chemical calculations. In particular, we are now equipped with the necessary means by which to calculate the exchange energies for 2-active electron systems and eventually 4-active electron systems, such as diatomic calcium Ca_2.

Appendix

A Double integrals over azimuth angles

In this appendix, we consider double integrals of functions $f(\phi_1, \phi_2)$ over the full range of both angles, i.e. $0 \le \phi_i \le 2\pi$ $(i = 1, 2)$. We do this first without further specification of the integrand. Subsequently, special cases, where the integrand involves a Legendre polynomial $P_l(\cos\omega)$, with $\omega = \phi_1 - \phi_2$, will be discussed in more detail.

A.1 General considerations

For later reference, we summarize a few results for the general case of a double integral I of a function $f(x, y)$ over a region with $0 \le x \le a$, $0 \le y \le a$ (i.e. a square-shaped region with sides of length a, see Fig. 1):

$$I = \int_0^a \mathrm{d}x \int_0^a \mathrm{d}y\, f(x,y) = \int_{-a/2}^{a/2} \mathrm{d}s \int_{-a/2}^{a/2} \mathrm{d}t\, \overline{f}(s,t) \tag{45}$$

$$= \frac{1}{2} \int_{-a}^{a} \mathrm{d}u \int_{|u|}^{2a-|u|} \mathrm{d}v\, g(u,v) = \frac{1}{2} \int_{-a}^{a} \mathrm{d}p \int_{-a+|p|}^{a-|p|} \mathrm{d}q\, \overline{g}(p,q) \tag{46}$$

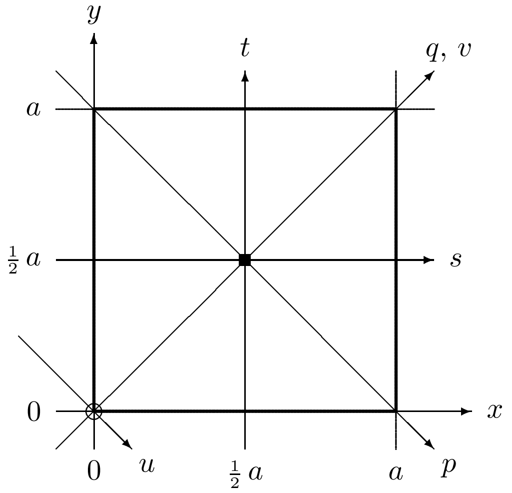
Various sets of Cartesian coordinates have been used here (see Fig. 1), and the corresponding integrands are connected to the initial $f(x, y)$ through the relations:

$$\overline{f}(s,t) = f\left(s + \tfrac{1}{2}\,a, t + \tfrac{1}{2}\,a\right) , \tag{47}$$

$$g(u,v) = f\left(\tfrac{1}{2}(u+v), -\tfrac{1}{2}(u-v)\right) , \tag{48}$$

$$\overline{g}(p,q) = f\left(\tfrac{1}{2}(p+q+a), -\tfrac{1}{2}(p-q-a)\right) . \tag{49}$$

In Fig. 1, the origin of the (x, y)- and (u, v)-coordinates is at the lower left edge of the square (marked by a circle), whereas the (s, t)- and (p, q)-coordinates have their origin at the center of the square (marked by a filled box).



Relations between the different coordinates:

(a) $x = s + \frac{1}{2}\,a = \frac{1}{2}(u+v)$,
$y = t + \frac{1}{2}\,a = -\frac{1}{2}(u-v)$

(b) $s = x - \frac{1}{2}\,a = \frac{1}{2}(p+q)$,
$t = y - \frac{1}{2}\,a = -\frac{1}{2}(p-q)$

(c) $u = x - y = s - t$,
$v = x + y = s + t + a$

(d) $p = u = x - y$,
$q = v - a = x + y - a$

Figure 1: Coordinate systems (a)-(d) used for double integrals over a square. See text for further details.

Of particular importance for the following is the case, where the integrand is a function of $p = u = x - y$ only. In this case we obtain, from eq. (45):

$$I = \int_0^a \mathrm{d}y \int_0^a \mathrm{d}x\, f(x-y) = \int_0^a \mathrm{d}y \int_{-y}^{a-y} \mathrm{d}u\, f(u) \tag{50}$$

If the function f is periodic with period a, $f(u+a) = f(u)$, the integral reduces to a one-dimensional integral, since integration of a periodic integrand over a full period is invariant with respect to the offset:

$$I = \left(\int_0^a \mathrm{d}y\right)\left(\int_0^a \mathrm{d}u\, f(u)\right) = a \int_0^a \mathrm{d}u\, f(u) \qquad (f \text{ is } a\text{-periodic}) \tag{51}$$

Starting, on the other hand, from eq. (46) leads to:

$$I = \int_{-a}^{a} \mathrm{d}u\, g(u)\,(a - |u|) = \begin{cases} 2\displaystyle\int_0^a \mathrm{d}u\, g(u)\,(a-u) & g \text{ even} \\ 0 & g \text{ odd} \end{cases} \tag{52}$$

where $g(u) = g(u,v)$. Again, a one-dimensional integral results, but with a linear factor in the integrand. The substitution $w = a - u$, together with the assumption $g(a-w) = g(w-a) = \varepsilon\, g(w)$, leads to

$$I = 2\,\varepsilon \int_0^a \mathrm{d}w\, w\, g(w) \qquad (g \text{ even}) \tag{53}$$

We rename the integration variable as u, and add this latter result to the expression in eq. (52), to obtain

$$2\,I = 2\int_0^a \mathrm{d}u\,(a - u + \varepsilon\, u)\, g(u) \qquad (g \text{ even}) \tag{54}$$

This leads, for periodic functions g, $g(u-a) = g(u)$, where $\varepsilon = +1$, to

$$I = a \int_0^a \mathrm{d}u\, g(u) \qquad (g \text{ even and } a\text{-periodic}) \tag{55}$$

which is almost equivalent to eq. (51), since $f(x-y) = f(u) = g(u)$ [see eq. (48)], with the only difference that eq. (55), as a part of eq. (52), also takes advantage of the parity property of the function g.

A.2 Double integrals with Legendre polynomials

The results from the previous section will now be applied to the special case, where $a = 2\pi$, $x = \phi_1$, $y = \phi_2$, $u = x - y = \phi_1 - \phi_2 = \omega$, and where the integrand involves a Legendre polynomial $P_l(\xi)$, with $\xi = \cos\omega$. The Legendre polynomials may be defined through Rodrigues' formula [13, 8.6.18],

$$P_l(\xi) = \frac{1}{(2l)!!}\left(\frac{\mathrm{d}}{\mathrm{d}\xi}\right)^l (\xi^2 - 1)^l \,, \tag{56}$$

where $k!!$ denotes the double factorial of k, defined recursively by $k!! = k \cdot (k-2)!!$, $(-1)!! = 0!! = 1$. An explicit expression for the Legendre polynomials is [13, 22.3.8]

$$P_l(\xi) = \sum_{k=0}^{[l/2]} p^{(l)}_{l-2k}\, \xi^{l-2k} \,, \quad p^{(l)}_{l-2k} = \frac{(-1)^k}{2^l}\binom{l}{k}\binom{2l-2k}{l} \,, \tag{57}$$

where we used $[x]$ to denote the largest integer less than or equal to x. For the special case $\xi = \cos\omega$, an expansion in terms of $\cos k\omega$ (k integer) is known, see e. g. [13, 22.3.13]:

$$P_l(\cos\omega) = \sum_{k=0}^{l} C^{(l)}_{l-2k}\, \cos{(l-2k)\omega} \,, \quad C^{(l)}_{l-2k} = \frac{1}{4^l}\binom{2k}{k}\binom{2l-2k}{l-k} \,, \tag{58}$$

or, equivalently, but now with restriction to *non-negative* multiples of ω as arguments of the cosines,

$$P_l(\cos\omega) = \sum_{k=0}^{[l/2]} (2 - \delta_{0,l-2k})\, C^{(l)}_{l-2k}\, \cos{(l-2k)\omega} \,. \tag{59}$$

We will now consider the following types of integrals (i, j, l, m, n are non-negative integers):

$$I_l = \int_0^{2\pi}\int_0^{2\pi} P_l(\cos\omega)\, \mathrm{d}\phi_1\, \mathrm{d}\phi_2 \tag{60}$$

$$J^c_{l,m} = \int_0^{2\pi}\int_0^{2\pi} P_l(\cos\omega)\, \cos m\omega\, \mathrm{d}\phi_1\, \mathrm{d}\phi_2 \tag{61}$$

$$J^s_{l,m} = \int_0^{2\pi}\int_0^{2\pi} P_l(\cos\omega)\, \sin m\omega\, \mathrm{d}\phi_1\, \mathrm{d}\phi_2 \tag{62}$$

$$K_{l,i,j} = \int_0^{2\pi}\int_0^{2\pi} P_l(\cos\omega)\, \cos^i\omega\, \sin^j\omega\, \mathrm{d}\phi_1\, \mathrm{d}\phi_2 \tag{63}$$

$$L_{l,m,i,j} = \int_0^{2\pi}\int_0^{2\pi} P_l(\cos\omega)\, \cos m\omega\, \cos^i\omega\, \sin^j\omega\, \mathrm{d}\phi_1\, \mathrm{d}\phi_2 \tag{64}$$

Some relations, which follow immediately from these definitions, are:

$$I_l = J^c_{l,0} = K_{l,0,0} = L_{l,0,0,0} \,; \tag{65}$$

$$J^c_{l,m} = L_{l,m,0,0} \,; \quad K_{l,i,j} = L_{l,0,i,j} \,; \quad K_{l,i+1,j} = L_{l,1,i,j} \,; \tag{66}$$

$$J^s_{l,0} = 0 \,; \quad J^c_{l,1} = K_{l,1,0} \,; \quad J^s_{l,1} = K_{l,0,1} \,. \tag{67}$$

Thus an explicit discussion of the integrals I_l, $J^c_{l,m}$, and $K_{l,i,j}$ is unnecessary, since they are all included as special cases of $L_{l,m,i,j}$. We will, however, keep the integrals $J^c_{l,m}$ as a simple intermediate case in the following. Application of eqs. (52) and (55) leads then to the following results for the remaining types of integrals:

$$J^c_{l,m} = 2\pi \int_0^{2\pi} \mathrm{d}\omega \, P_l(\cos\omega) \, \cos m\omega \tag{68}$$

$$J^s_{l,m} = \int_{-2\pi}^{2\pi} \mathrm{d}\omega \, (2\pi - |\omega|) \, P_l(\cos\omega) \, \sin m\omega = 0 \tag{69}$$

$$L_{l,m,i,j} = \frac{1}{2} \left[1 + (-1)^j\right] \, 2\pi \int_0^{2\pi} \mathrm{d}\omega \, P_l(\cos\omega) \, \cos m\omega \, \cos^i\omega \, \sin^j\omega \tag{70}$$

Thus all the integrals $J^s_{l,m}$ are zero, due to the factor $\sin m\omega$ in the integrand (this factor in the integrand leads, in general, to vanishing integrals over a symmetric integration range). In the case of $L_{l,m,i,j}$ a parity factor has been introduced, which makes the integral vanish for odd j ('odd integrand'), but gives one for even j ('even integrand').

The two remaining types of non-vanishing integrals, $J^c_{l,m}$ and $L_{l,m,i,j}$, are discussed in more detail in the remaining part of this section.

The integrals $J^c_{l,m}$

These integrals can be rewritten as

$$J^c_{l,m} = 2\pi \int_0^{2\pi} \mathrm{d}\omega \, P_l(\cos\omega) \, T_m(\cos\omega) \, , \tag{71}$$

where $T_m(\cos\omega) = \cos m\omega$ denotes the Chebyshev polynomial of the first kind of degree m in the variable $\cos\omega$ [13, 22.3.15]. An explicit expression for the Chebyshev polynomials is known (from [13, 22.3.6], modified to give correctly $t^{(0)}_0 = 1$),

$$T_m(\xi) = \sum_{q=0}^{[m/2]} t^{(m)}_{m-2q} \, \xi^{m-2q} \, , \quad t^{(m)}_{m-2q} = (-1)^q (1 + \delta_{0,m}) \, \frac{m}{2} \, \frac{(m-q-1)!}{q!(m-2q)!} \, 2^{m-2q} \, . \tag{72}$$

In eq. (71), we now substitute $\omega = \pi + \tau$ ($\cos\omega = -\cos\tau$) to reduce the range of integration finally to $0 \le \tau \le \pi$:

$$J^c_{l,m} = 2\pi \int_{-\pi}^{\pi} \mathrm{d}\tau \, P_l(-\cos\tau) \, T_m(-\cos\tau) \tag{73}$$

$$= 4\pi \, (-1)^{l+m} \int_0^{\pi} \mathrm{d}\tau \, P_l(\cos\tau) \, T_m(\cos\tau) \tag{74}$$

The parity relations $P_l(-x) = (-1)^l \, P_l(x)$ and $T_m(-x) = (-1)^m \, T_m(x)$ [13, Table 22.4], as well as the fact that the integrand is an even function of τ have been used here. The substitution $\cos\tau = t$ leads then to the result

$$J^c_{l,m} = 4\pi \, (-1)^{l+m} \int_{-1}^{1} \mathrm{d}t \, \frac{P_l(t) \, T_m(t)}{\sqrt{1-t^2}} \tag{75}$$

$$= 4\pi \, (-1)^{l+m} \, \frac{1}{2} \left[1 + (-1)^{l+m}\right] \int_{-1}^{1} \mathrm{d}t \, \frac{P_l(t) \, T_m(t)}{\sqrt{1-t^2}} \tag{76}$$

The factor introduced in the last step makes the integral vanish, if the integrand is of odd symmetry (the prefactor $(-1)^{l+m}$ is ineffective and could be omitted, but is kept for completeness).

With eq. (59), a closed form for $J^c_{l,m}$ is accessible, either by direct use of that expansion with eq. (71) and by taking advantage of the formula $\int_0^{2\pi} \cos mx \, \cos nx \, \mathrm{d}x = \pi \, (1 + \delta_{0,m}) \, \delta_{m,n}$ [22, 32:10:26], or by first rewriting that expansion in terms of the Chebyshev polynomials and subsequent application of the orthogonality relation $\int_{-1}^{1}(1-t^2)^{-1/2}\,T_m(t)\,T_n(t)\,\mathrm{d}t=\frac{\pi}{2}\,(1+\delta_{0,m})\,\delta_{m,n}$ [22, 22:10:4]. Both ways lead to

$$J^c_{l,m}=\pi^2\,(-1)^{l+m}\,\Big[1+(-1)^{l+m}\Big]\,(1+\delta_{0,m})\sum_{k=0}^{[l/2]}(2-\delta_{0,l-2k})\,\delta_{l-2k,m}\,C^{(l)}_{l-2k}\,, \tag{77}$$

so that the integral $J^c_{l,m}$, firstly, gives zero whenever $l+m$ is odd or $l<m$ (see Fig. 2), and, secondly, reduces to one of the coefficients $C^{(l)}_{l-2k}$, times a multiple of π^2, in all other cases. We briefly discuss some special cases of eq. (77):

(a) $m=0$: The integral $J^c_{l,0}=I_l$ is zero for odd l, while for even l the sum reduces to the term with $l-2k=0$, thus

$$\begin{aligned}
J^c_{l,0}&=2\pi\int_0^{2\pi}\mathrm{d}\omega\,P_l(\cos\omega)\\
&=2\pi\,(-1)^l\,\Big[1+(-1)^l\Big]\int_{-1}^{1}\mathrm{d}t\,\frac{P_l(t)}{\sqrt{1-t^2}}\\
&=2\pi^2\,\Big[1+(-1)^l\Big]\,C^{(l)}_0=\begin{cases}\dfrac{4\pi^2}{4^{2k}}\dbinom{2k}{k}^2 & l=2k\\ 0 & l=2k+1\end{cases}
\end{aligned} \tag{78}$$

which is consistent with results from the literature, e.g. [13, 22.13.6], [22, 21:10:5], [20, 7.221.3 & 7.226.1]:

$$\begin{aligned}
&\int_0^{\pi}P_{2n}(\cos\vartheta)\,\mathrm{d}\vartheta=\frac{\pi}{16^n}\binom{2n}{n}^2\\
&\int_0^{2\pi}P_{2n}(\cos\varphi)\,\mathrm{d}\varphi=2\pi\left[\binom{2n}{n}2^{-2n}\right]^2\\
&\int_{-1}^{1}\frac{P_n(t)}{\sqrt{1-t^2}}\,\mathrm{d}t=\begin{cases}\pi\left[\dfrac{(n-1)!!}{n!!}\right]^2 & n=0,2,4,\ldots\\ 0 & n=1,3,5,\ldots\end{cases}\\
&\int_{-1}^{1}(1-t^2)^{-1/2}\,P_{2m}(t)\,\mathrm{d}t=\left[\frac{1}{m!}\,\Gamma\left(\frac{1}{2}+m\right)\right]^2
\end{aligned}$$

(b) $m=1$: The integral $J^c_{l,1}$ is zero for even l, while for odd l the sum reduces to the term with $l-2k=1$, thus

$$\begin{aligned}
J^c_{l,1}&=2\pi\int_0^{2\pi}\mathrm{d}\omega\,P_l(\cos\omega)\,\cos\omega\\
&=2\pi\,(-1)^{l+1}\,\Big[1+(-1)^{l+1}\Big]\int_{-1}^{1}\mathrm{d}t\,\frac{t\,P_l(t)}{\sqrt{1-t^2}}\\
&=2\pi^2\,\Big[1+(-1)^{l+1}\Big]\,C^{(l)}_1=\begin{cases}0 & l=2k\\ \dfrac{4\pi^2}{4^{2k+1}}\dbinom{2k}{k}\dbinom{2k+2}{k+1} & l=2k+1\end{cases}
\end{aligned} \tag{79}$$

in accordance with results from the literature, e.g. [13, 22.13.7], [20, 7.245.1 & 7.226.2]:

$$\begin{aligned}
&\int_0^{\pi}P_{2n+1}(\cos\vartheta)\,\cos\vartheta\,\mathrm{d}\vartheta=\frac{\pi}{4^{2n+1}}\binom{2n}{n}\binom{2n+2}{n+1}\\
&\int_0^{2\pi}P_{2m+1}(\cos\varphi)\,\cos\varphi\,\mathrm{d}\varphi=\frac{\pi}{2^{4m+1}}\binom{2m}{m}\binom{2m+2}{m+1}\\
&\int_{-1}^{1}t\,(1-t^2)^{-1/2}\,P_{2m+1}(t)\,\mathrm{d}t=\frac{1}{m!(m+1)!}\,\Gamma\left(\frac{1}{2}+m\right)\,\Gamma\left(\frac{3}{2}+m\right)
\end{aligned}$$

(c) $m = l$: The integral $J^c_{l,l}$ is always non-zero, only the term with $k = 0$ contributes to the sum, thus

$$\begin{aligned} J^c_{l,l} &= 2\pi \int_0^{2\pi} \mathrm{d}\omega\, P_l(\cos\omega)\, T_l(\cos\omega) = 4\pi \int_{-1}^{1} \mathrm{d}t\, \frac{P_l(t)\, T_l(t)}{\sqrt{1-t^2}} \\ &= 2\pi^2\,(1+\delta_{0,l})\,(2-\delta_{0,l})\, C_l^{(l)} = 4\pi^2\, C_l^{(l)} = \frac{4\pi^2}{4^l}\binom{2l}{l} \end{aligned} \tag{80}$$

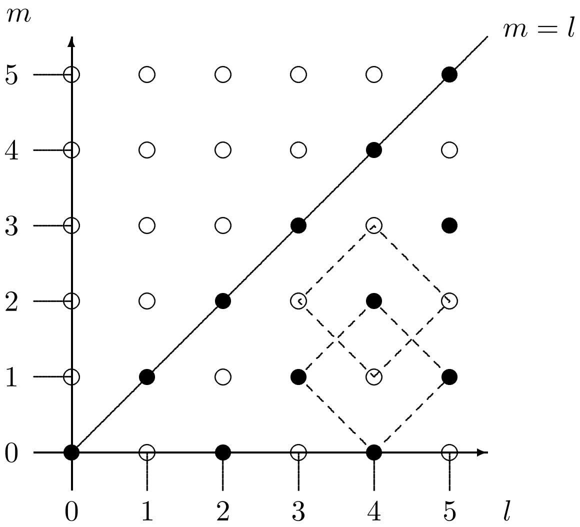


Figure 2: Graphical representation of a part of the array of integrals $J^c_{l,m}$ (open circle: $J^c_{l,m} = 0$, filled circle: $J^c_{l,m} \neq 0$). Points representing integrals related through the recurrence relation eq. (81) are connected by dashed lines. See text for further details.

We include also a recurrence relation for $J^c_{l,m}$,

$$J^c_{l,m} = \frac{2l+2}{2l+1}\, J^c_{l+1,m-1} + \frac{2l}{2l+1}\, J^c_{l-1,m-1} - J^c_{l,m-2}\,, \tag{81}$$

which is obtainable e.g. from eq. (71) and the well known recurrence relations for the polynomials [13, Table 22.7],

$$T_n(\xi) - 2\,\xi\, T_{n-1}(\xi) + T_{n-2}(\xi) = 0 \qquad (n = 2, 3, \ldots)\,, \tag{82}$$

$$(l+1)\, P_{l+1}(\xi) - (2l+1)\,\xi\, P_l(\xi) + l\, P_{l-1}(\xi) = 0 \qquad (l = 1, 2, \ldots)\,, \tag{83}$$

replacing first $T_m(\xi)$ by use of the first of these equations, and removing then the $\xi\, P_l(\xi)$ with the help of the second equation ($\xi = \cos\omega$). A graphical representation for the integrals related through eq. (81) is given in Fig. 2. All integrals $J^c_{l,m}$ can be calculated easily from eq. (78) and eq. (81). For this purpose, we set $J^c_{l,m} = 0$ whenever $m > l$ (formally used even for negative l), and rewrite the recurrence relation as

$$J^c_{l,m} = \frac{2l-1}{2l}\,\left\{J^c_{l-1,m+1} + J^c_{l-1,m-1}\right\} - \frac{2l-2}{2l}\, J^c_{l-2,m} \tag{84}$$

If we consider the ratio $J^c_{l,m}/J^c_{0,0}$ ($J^c_{0,0} = 4\pi^2$), instead of $J^c_{l,m}$, eq. (81) gives a recurrence relation for pure rational numbers. Even a recursion for integers is possible, if we rescale the polynomials $P_l(\xi)$, and equivalently $J^c_{l,m}$, to give:

$$\widetilde{J}^c_{l,m} = \frac{1}{4}\,\frac{2l+2}{2l+1}\, \widetilde{J}^c_{l+1,m-1} + 4\,\frac{2l}{2l+1}\, \widetilde{J}^c_{l-1,m-1} - \widetilde{J}^c_{l,m-2}\,, \tag{85}$$

where $\widetilde{J}^c_{l,m} = 4^l\, J^c_{l,m}/J^c_{0,0}$ is an integer. A disadvantage of eq. (85) is that $\widetilde{J}^c_{l,m} \to \infty$ as $l \to \infty$, whereas for eq. (81) $J^c_{l,m} \to 0$ as $l \to \infty$ (these limits hold for any m).

The integrals $L_{l,m,i,j}$

The expression given by eq. (70) can be rewritten as

$$L_{l,m,i,j} = \pi \, \left[1 + (-1)^j\right] \int_0^{2\pi} \mathrm{d}\omega \, P_l(\cos\omega) \, T_m(\cos\omega) \, \cos^i \omega \, \sin^j \omega \tag{86}$$

We proceed by substituting first $\omega = \pi + \tau$, and then, in a second step, $\cos\tau = t$, so that the following equivalent expressions are obtained:

$$\begin{aligned} L_{l,m,i,j} &= \pi \, \left[1 + (-1)^j\right]^2 (-1)^{l+m+i+j} \\ &\quad \times \int_0^{\pi} \mathrm{d}\tau \, P_l(\cos\tau) \, T_m(\cos\tau) \, \cos^i \tau \, \sin^j \tau \qquad (87) \\ &= \pi \, \left[1 + (-1)^j\right]^2 (-1)^{l+m+i+j} \frac{1}{2} \left[1 + (-1)^{l+m+i+j}\right] \\ &\quad \times \int_{-1}^{1} \mathrm{d}t \, P_l(t) \, T_m(t) \, t^i \, (1 - t^2)^{(j-1)/2} \qquad (88) \end{aligned}$$

To obtain an explicit expression for $L_{l,m,i,j}$, we return to eq. (86), and use the expansions eq. (57) and eq. (72) for the polynomials (with $\xi = \cos\omega$), together with the formula [24]

$$\int_0^{2\pi} \cos^k x \, \sin^l x \, \mathrm{d}x = \frac{1}{2} \left[1 + (-1)^k\right] \left[1 + (-1)^l\right] B\left(\frac{k+1}{2}, \frac{l+1}{2}\right) \tag{89}$$

where $B(a,b) = \Gamma(a)\Gamma(b)/\Gamma(a+b)$ denotes the Euler beta function (this formula is easily obtainable from the integral representation of the beta function, [13, 6.2.1], and general rules for reducing the integration range of definite integrals of the type $\int_0^{2\pi} f(\cos x, \sin x)\,\mathrm{d}x$ [18, 2.1.2.83]). This gives $L_{l,m,i,j}$ as a finite sum of values of the beta function, which can be written as:

$$\begin{aligned} L_{l,m,i,j} &= \pi \, \left[1 + (-1)^j\right] \sum_{u=0}^{\max(u)} a_{l+m-2u} \int_0^{2\pi} \mathrm{d}\omega \, \cos^{l+m+i-2u} \omega \, \sin^j \omega \qquad (90) \\ &= \frac{\pi}{2} \, \left[1 + (-1)^j\right]^2 \left[1 + (-1)^{l+m+i}\right] \Gamma\left(\frac{j+1}{2}\right) \\ &\quad \times \sum_{u=0}^{\max(u)} a_{l+m-2u} \frac{\Gamma\left(\frac{l+m+i+1}{2} - u\right)}{\Gamma\left(\frac{l+m+i+j+2}{2} - u\right)} \qquad (91) \end{aligned}$$

where $\max(u) = [l/2] + [m/2]$, and where a_{l+m-2u} denotes the coefficient of ξ^{l+m-2u} in the product of the Legendre polynomial $P_l(\xi)$ and the Chebyshev polynomial $T_m(\xi)$. Our result also shows, that the integrals $L_{l,m,i,j}$ are necessarily zero, if $l + m + i$ is an odd integer.

It is instructive to outline another route to an explicit expression for $L_{l,m,i,j}$. We consider the following expansions (from [22, 32:5:17 & 32:5:18])

$$\cos^i x = \sum_{p=0}^{i} c_{i-2p}^{(i)} \cos\left[(i-2p)x\right] = \sum_{p=0}^{[i/2]} (2 - \delta_{0,i-2p}) \, c_{i-2p}^{(i)} \, T_{i-2p}(\cos x) \tag{92}$$

$$\sin^j x = \sum_{q=0}^{j} s_{j-2q}^{(j)} \cos\left[(j-2q)x\right] = \sum_{q=0}^{[j/2]} (2 - \delta_{0,j-2q}) \, s_{j-2q}^{(j)} \, T_{j-2q}(\cos x) \tag{93}$$

$$c_{i-2p}^{(i)} = \frac{1}{2^i}\binom{i}{p}, \qquad s_{j-2q}^{(j)} = \frac{(-1)^{q+j/2}}{2^j}\binom{j}{q}$$

Then it follows from these two expansions, and eq. (59), in connection with the relation $2\,T_m(x)\,T_n(x) = T_{m+n}(x) + T_{|m-n|}(x)$ [13, 22.7.24], that we can write

$$P_l(\cos\omega)\,\cos^i\omega\,\sin^j\omega = \sum_{v=0}^{l+i+j} b_v\,T_v(\cos\omega)\,, \tag{94}$$

where the coefficients b_v are essentially sums of products of the coefficients $C^{(l)}_{l-2k}$, $c^{(i)}_{i-2p}$, and $s^{(j)}_{j-2q}$. We combine eq. (94) with eq. (86), to obtain

$$\begin{aligned} L_{l,m,i,j} &= \pi\,\left[1+(-1)^j\right] \sum_{v=0}^{l+i+j} b_v \int_0^{2\pi} \mathrm{d}\omega\,T_m(\cos\omega)\,T_v(\cos\omega) \\ &= \pi^2\,(1+\delta_{0,m})\,\left[1+(-1)^j\right] \sum_{v=0}^{l+i+j} \delta_{m,v}\,b_v \end{aligned} \tag{95}$$

Hence it follows that the integrals $L_{l,m,i,j}$ also vanish if $m > l+i+j$ (see Fig. 3). In all other cases, the integral is essentially given by a single coefficient b_v, which might itself be zero, e.g. if m and $l+i+j$ have different parity. We note that there occur also ‘accidental zeros’, e.g. $L_{1,2,1,2} = 0$, which should be non-zero according to the rules given above.

Various recurrence relations for $L_{l,m,i,j}$ exist. Application of the relation $\sin^2 x + \cos^2 x = 1$ leads to

$$L_{l,m,i,j} = L_{l,m,i-2,j} - L_{l,m,i-2,j+2} = L_{l,m,i,j-2} - L_{l,m,i+2,j-2}\,, \tag{96}$$

where both l and m remain constant. The recurrence relations for the polynomials, eq. (82) and eq. (83), may be used either separately, to yield

$$L_{l,m,i,j} = 2\,L_{l,m-1,i+1,j} - L_{l,m-2,i,j} \tag{97}$$

$$= \frac{2l-1}{l}\,L_{l-1,m,i+1,j} - \frac{l-1}{l}\,L_{l-2,m,i,j}\,, \tag{98}$$

so that either l or m can be kept constant, or in a combined manner, as for $J^c_{l,m}$ above, to give

$$L_{l,m,i,j} = \frac{2l+2}{2l+1}\,L_{l+1,m-1,i,j} + \frac{2l}{2l+1}\,L_{l-1,m-1,i,j} - L_{l,m-2,i,j}\,, \tag{99}$$

which is the equivalent of eq. (81) above, and leaves both i and j unchanged. We briefly discuss a few simple cases of the integrals $L_{l,m,i,j}$ (where j is always assumed to be even), based on eqs. (86), (57), (72), and (89):

(a) $m = 0$: The integrals $L_{l,0,i,j} = K_{l,i,j}$ are

$$\begin{aligned} L_{l,0,i,j} &= 2\pi \int_0^{2\pi} \mathrm{d}\omega\,P_l(\cos\omega)\,\cos^i\omega\,\sin^j\omega \\ &= 2\pi\,\left[1+(-1)^{l+i}\right] \sum_{k=0}^{[l/2]} p^{(l)}_{l-2k}\,B\left(\frac{l+i+1-2k}{2}, \frac{j+1}{2}\right) \end{aligned} \tag{100}$$

(b) $m = 1$: The integrals $L_{l,1,i,j} = K_{l,i+1,j}$ are

$$\begin{aligned} L_{l,1,i,j} &= 2\pi \int_0^{2\pi} \mathrm{d}\omega\,P_l(\cos\omega)\,\cos^{i+1}\omega\,\sin^j\omega \\ &= 2\pi\,\left[1+(-1)^{l+i+1}\right] \sum_{k=0}^{[l/2]} p^{(l)}_{l-2k}\,B\left(\frac{l+i+2-2k}{2}, \frac{j+1}{2}\right) \end{aligned} \tag{101}$$

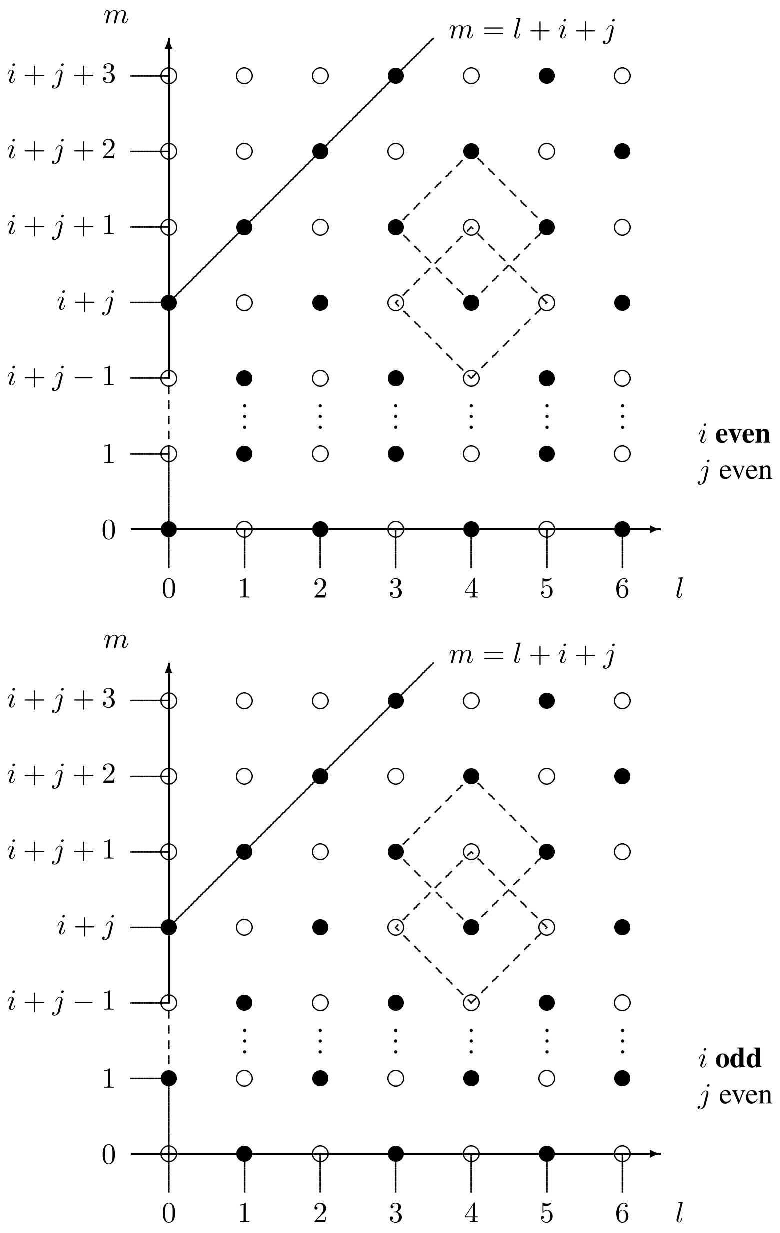


Figure 3: Graphical representation of a part of the array of integrals $L_{l,m,i,j}$ (j always even, open circle: $L_{l,m,i,j} = 0$, filled circle: $L_{l,m,i,j} \neq 0$). Top: i even, bottom: i odd. Points representing integrals related through the recurrence relation eq. (99) are connected by dashed lines. See text for further details.

(c) $l = 0$: The integrals $L_{0,m,i,j}$ are

$$\begin{aligned} L_{0,m,i,j} &= 2\pi \int_0^{2\pi} \mathrm{d}\omega\, T_m(\cos\omega)\, \cos^i \omega\, \sin^j \omega \\ &= 2\pi\, \left[1 + (-1)^{m+i}\right] \sum_{q=0}^{[m/2]} t_{m-2q}^{(m)}\, B\left(\frac{m+i+1-2q}{2}, \frac{j+1}{2}\right) \end{aligned} \tag{102}$$

(d) $l = 1$: The integrals $L_{1,m,i,j}$ are

$$\begin{aligned} L_{1,m,i,j} &= 2\pi \int_0^{2\pi} \mathrm{d}\omega \, T_m(\cos\omega) \, \cos^{i+1}\omega \, \sin^j \omega \\ &= 2\pi \left[1 + (-1)^{m+i+1}\right] \sum_{q=0}^{[m/2]} t_{m-2q}^{(m)} \, B\left(\frac{m+i+2-2q}{2}, \frac{j+1}{2}\right) \end{aligned} \tag{103}$$

Special cases included here are the integrals

$$\begin{aligned} L_{0,0,i,j} &= 2\pi \int_0^{2\pi} \mathrm{d}\omega \, \cos^i \omega \, \sin^j \omega = 2\pi \left[1 + (-1)^i\right] B\left(\frac{i+1}{2}, \frac{j+1}{2}\right) \\ &= \begin{cases} 4\pi^2 \, \dfrac{(2k-1)!!(2l-1)!!}{2^{k+l}(k+l)!} & i = 2k\,, \; j = 2l \\ 0 & \text{otherwise} \end{cases} \end{aligned} \tag{104}$$

$$\begin{aligned} L_{0,1,i,j} &= L_{1,0,i,j} \\ &= 2\pi \int_0^{2\pi} \mathrm{d}\omega \, \cos^{i+1} \omega \, \sin^j \omega = 2\pi \left[1 + (-1)^{i+1}\right] B\left(\frac{i+2}{2}, \frac{j+1}{2}\right) \\ &= \begin{cases} 4\pi^2 \, \dfrac{(2k+1)!!(2l-1)!!}{2^{k+l+1}(k+l+1)!} & i = 2k+1\,, \; j = 2l \\ 0 & \text{otherwise} \end{cases} \end{aligned} \tag{105}$$

$$\begin{aligned} L_{1,1,i,j} &= 2\pi \int_0^{2\pi} \mathrm{d}\omega \, \cos^{i+2} \omega \, \sin^j \omega = 2\pi \left[1 + (-1)^i\right] B\left(\frac{i+3}{2}, \frac{j+1}{2}\right) \\ &= \begin{cases} 4\pi^2 \, \dfrac{(2k+1)!!(2l-1)!!}{2^{k+l+1}(k+l+1)!} & i = 2k\,, \; j = 2l \\ 0 & \text{otherwise} \end{cases} \end{aligned} \tag{106}$$

With these results, which can be considered also as special cases of eq. (91), and with the previously given recurrence relations, all integrals $L_{l,m,i,j}$ can be evaluated recursively. If, in particular, i and j are given, then the evaluation can be based on eq. (99), just in the same way as demonstrated previously for the integrals $J^c_{l,m}$. The recurrence relations may be rescaled to the quantities $L_{l,m,i,j}/L_{0,0,0,0}$ ($L_{0,0,0,0} = 4\pi^2$), to involve only rational numbers.

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