Canonical density matrix for free electrons moving on a spherical surface

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The energy levels and eigenfunctions for electrons that are confined to moving on the surface of a sphere but are otherwise free are utilized to calculate the corresponding canonical density matrix. This matrix is then expanded in an asymptotic series for a large sphere radius R. The leading term naturally corresponds to free electrons moving on a plane and the first correction term to this, $O(R^{-2})$, is exhibited explicitly. This matrix is then utilized to construct both the Dirac density matrix and the Green function in the same approximation. This Green function, in relation, say, to K-doped C_{60}, where added electrons are localized near the surface of a sphere, serves to emphasize first the quasi-two-dimensional character of the motion, and then to exhibit the corrections for a finite ball radius.

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I. INTRODUCTION

There is now good evidence that if solid C_{60} is doped with an alkali metal, say K, the donated electrons are rather localized near the surface of the molecule [1,2]. This has motivated us to consider a model problem of electrons confined to move on the surface of a sphere of radius R but otherwise free. This model has also been treated by Gedik and Ciraci [3]. However, whereas these workers were concerned with approximating the Green function for small energy, our focus here is the canonical density matrix, defined precisely in Eq. (1.1) below. This is intimately related to the Feynman propagator, where the variable β in the Bloch equation (1.2) is replaced by $it/\hbar$, with t the time. We shall first give an exact expression for the canonical density matrix in Sec. II, while in Sec. III an asymptotic expansion is developed for a large sphere radius. This result is then utilized in Sec. IV to obtain an analogous expansion for the Dirac density matrix, while Sec. V gives the corresponding Green function.

First, however, let us summarize the definition of the canonical density matrix C for a system of independent electrons described by a one-electron Hamiltonian $\mathcal{H}_{\mathbf{r}}$. Suppose the eigenfunctions of $\mathcal{H}_{\mathbf{r}}$ are $\psi_j(\mathbf{r})$ with corresponding eigenvalues ϵ_j. Then the canonical density matrix $C(\mathbf{r}_1,\mathbf{r}_2;\beta)$ is defined as

$$C(\mathbf{r}_1,\mathbf{r}_2;\beta)=\sum_{\text{all } j}\psi_j(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\exp(-\beta\epsilon_j) , \qquad (1.1)$$

where β, complex in general, can be thought of formally as a time variable, or, alternatively, in statistical mechanical language, as $(k_BT)^{-1}$. From the Schrödinger equation, it then follows that C satisfies the Bloch equation

$$\mathcal{H}_{\mathbf{r}}C(\mathbf{r},\mathbf{r}';\beta)=-\frac{\partial C(\mathbf{r},\mathbf{r}';\beta)}{\partial\beta} \qquad (1.2)$$

with the condition for the completeness of the set of eigenfunctions $\psi_j(\mathbf{r})$ being embodied in the boundary condition

$$C(\mathbf{r}_1,\mathbf{r}_2;\beta=0)=\delta(\mathbf{r}_1-\mathbf{r}_2) . \qquad (1.3)$$

In our recent paper [4], one can find references to earlier use of C in condensed matter studies, as well as results concerning this matrix for free electrons moving in D-dimensional Cartesian space, with arbitrary D.

Below, we shall exhibit explicitly the exact solution of Eq. (1.2) satisfying the condition (1.3) for the admittedly very simple model problem of free electrons moving on a spherical surface.

II. CANONICAL DENSITY MATRIX FOR THE SPHERE MODEL

First, let us set down the solutions of the Schrödinger equation for free electrons moving on the surface of a sphere of radius R. To do so, we recall this equation for the free-electron Hamiltonian $\mathcal{H}_0$ in three-dimensional (3D) space in spherical polar coordinates (r,θ,ϕ), namely,

$$\mathcal{H}_0\psi=\frac{\hbar^2}{2m_e}\left[-\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right]+\frac{\hat{l}^2}{r^2}\psi\right]=\epsilon\psi , \qquad (2.1)$$

where the operator $\hat{l}^2$ acts on coordinates θ,ϕ only. Its eigenequation

$$\hat{l}^2Y_{lm}(\theta,\phi)=l(l+1)Y_{lm}(\theta,\phi) ,$$
$$l=0,1,2,\ldots,\quad m=-l,-l+1,\ldots,l , \qquad (2.2)$$

is solved in terms of the spherical harmonics, obeying the orthogonality and normalization

$$\int_{4\pi}d^2\Omega\, Y_{lm}^*(\Omega)Y_{l'm'}(\Omega)=\delta_{ll'}\delta_{mm'} \qquad (2.3)$$

and closure relations

$$\sum_{l,m} Y^*_{lm}(\Omega)Y_{lm}(\Omega')=\delta(\Omega-\Omega') . \tag{2.4}$$

Assuming that electrons are allowed to move only on the surface of the sphere, $\psi(r,\theta,\phi)$ is to be replaced by $\psi(R,\theta,\phi)$ while differentiations with respect to r are to be set equal to zero. Hence Eq. (2.1) for the present model is then reduced to read

$$\frac{\hbar^2}{2m_e}\frac{\hat{l}^2}{R^2}\psi(R,\theta,\phi)=\epsilon\psi(R,\theta,\phi) \tag{2.5}$$

with solution, according to Eq. (2.2):

$$\psi_{lm}=\frac{1}{R}Y_{lm}(\theta,\phi) , \quad \epsilon_{lm}=\epsilon_l=\frac{\hbar^2 l(l+1)}{2m_eR^2} \tag{2.6}$$

normalized on the spherical surface such that

$$\int_{4\pi R^2} d^2S\, \psi^*_{lm}\psi_{l'm'}=\int_{4\pi} R^2 d^2\Omega \frac{Y^*_{lm}}{R}\frac{Y_{l'm'}}{R} =\delta_{ll'}\delta_{mm'} . \tag{2.7}$$

It is to be noted that this normalization remains meaningful in the $R\to\infty$ limit (i.e., the flat 2D case).

Introducing as the unit for the kinetic energy on the sphere:

$$E_R=\frac{\hbar^2}{2m_eR^2} , \tag{2.8}$$

the eigenenergy in Eq. (2.6) may be rewritten as

$$\epsilon_l=E_R l(l+1) . \tag{2.9}$$

This is the point to return to the general definition (1.1) and to note, since in the present case $j=(l,m)$, that the canonical density matrix of the model becomes

$$C_0^{(R)}(\mathbf{r}_1,\mathbf{r}_2;\beta)=\sum_{l=0}^{\infty}\exp[-\beta E_R l(l+1)] \times \sum_{m=-l}^{l} R^{-2}Y_{lm}(\theta_1,\phi_1)Y^*_{lm}(\theta_2,\phi_2) , \tag{2.10}$$

where

$$\mathbf{r}_i=R\mathbf{n}_i , \quad |\mathbf{n}_i|=1 , \quad \mathbf{n}_i=\mathbf{n}(\theta_i,\phi_i) , \quad i=1,2 . \tag{2.11}$$

Due to the closure relation (2.4), the boundary condition (1.3) is fulfilled by $C_0^{(R)}$ given in Eq. (2.10). The second sum in Eq. (2.10) is known to be

$$\sum_{m=-l}^{l} Y_{lm}(\mathbf{n}_1)Y^*_{lm}(\mathbf{n}_2)=(2l+1)(4\pi)^{-1}P_l(\mathbf{n}_1\cdot\mathbf{n}_2) , \tag{2.12}$$

where $P_l(z)$ is the Legendre polynomial. Using the definition (2.11), we obtain for its argument in Eq. (2.12):

$$\mathbf{n}_1\cdot\mathbf{n}_2=1-2\left[\frac{s}{2R}\right]^2 , \quad 0\le\left[\frac{s}{2R}\right]^2\le 1 , \tag{2.13}$$

where

$$s=|\mathbf{r}_1-\mathbf{r}_2| . \tag{2.14}$$

After substituting Eq. (2.13) in Eq. (2.12) and further into Eq. (2.10), we then find

$$C_0^{(R)}(\mathbf{r}_1,\mathbf{r}_2;\beta)\equiv C_0^{(R)}(|\mathbf{r}_1-\mathbf{r}_2|=s\ ;\beta) =(4\pi R^2)^{-1}\sum_{l=0}^{\infty}\exp[-\beta E_R l(l+1)](2l+1)P_l\left[1-2\left[\frac{s}{2R}\right]^2\right] . \tag{2.15}$$

The result (2.15) represents the exact canonical density matrix for free electrons moving on the spherical surface of radius R. Its form corresponds precisely to the result of Gedik and Ciraci [3] for the Green function of the same model [see definition (5.1) below].

III. EXPANSION OF CANONICAL DENSITY MATRIX (2.15) FOR LARGE R

Our main aim below is now to demonstrate that the sum over l in Eq. (2.15) can, in fact, be carried out in the limit of large R. Specifically, it will be shown that $C_0^{(R)}(s;\beta)$ in Eq. (2.15) can be evaluated in closed form as an asymptotic series in powers of R^{-2}.

The first step in the derivation is to find a representation of P_l, appropriate for its argument exhibited in Eq. (2.15). Writing P_l in terms of the hypergeometric function $F(\alpha,\beta;\gamma;z)$ as

$$P_l(1-2x)=F(-l,l+1;1;x) , \tag{3.1}$$

we have it as a polynomial of lth order in x, namely,

$$P_l(1-2x)=\sum_{n=0}^{l}(-1)^n p_{ln}x^n , \tag{3.2}$$

where

$$p_{l0}=1 , \quad p_{ln}=\frac{1}{(n!)^2}\prod_{j=1-n}^{n}(l+j) , \quad n=1,2,\ldots,l . \tag{3.3}$$

Utilizing this result, Eq. (2.15) can be rewritten as

$$C_0^{(R)}(s;\beta)=(4\pi R^2)^{-1}\sum_{l=0}^{\infty}\exp[-\beta E_R l(l+1)](2l+1) \times\sum_{n=0}^{l} p_{ln}\left[-\left[\frac{s}{2R}\right]^2\right]^n . \tag{3.4}$$

Next, the change in the order of the summation over l and n in Eq. (3.4) can be carried out because of the finite range of n there:

$$C_0^{(R)}(s;\beta)=(4\pi R^2)^{-1}\sum_{n=0}^{\infty}\left[-\left[\frac{s}{2R}\right]^2\right]^n \times\sum_{l=n}^{\infty}(2l+1)p_{ln} \times\exp[-\beta E_R l(l+1)] \ . \quad (3.5)$$

Introducing the parameter

$$\xi^2=\beta E_R=\frac{\tilde{\beta}}{2R^2} \ , \quad (3.6)$$

where

$$\tilde{\beta}=\beta\hbar^2/m_e \quad (3.7)$$

has dimensions of length squared, we can rewrite Eq. (3.5), by multiplying and dividing it by $n!\xi^{2(n+1)}$ and making use of Eq. (3.3), to obtain

$$C_0^{(R)}(s;\beta)=(2\pi\tilde{\beta})^{-1}\sum_{n=0}^{\infty}\frac{1}{n!}\left[-\frac{s^2}{2\tilde{\beta}}\right]^n Q_n(\tilde{\beta}/2R^2) \ , \quad (3.8)$$

where

$$Q_n(\xi^2)=\frac{2}{n!}\sum_{l=n}^{\infty}\exp[-\xi^2 l(l+1)]\xi^{2(n+1)}(l+\tfrac{1}{2}) \times\prod_{j=1-n}^{n}(l+j) \ . \quad (3.9)$$

This result (3.8) is still exact for the sphere model. It is to be noted that the dependence on R enters via the argument of Q_n.

In the Appendix we evaluate $Q_n(\xi^2)$ as an asymptotic power series in ξ^2. The result derived there is

$$Q_n(\xi^2)\simeq 1+\tfrac{1}{3}(1-n^2)\xi^2+O(\xi^4) \ , \quad (3.10)$$

which inserted into Eq. (3.8) yields

$$C_0^{(R)}(s;\beta)\simeq(2\pi\tilde{\beta})^{-1}\sum_{n=0}^{\infty}\frac{1}{n!}\left[-\frac{s^2}{2\tilde{\beta}}\right]^n \times\left[1+\tfrac{1}{3}(1-n^2)\frac{\tilde{\beta}}{2R^2} +O\left[\left[\frac{\tilde{\beta}}{2R^2}\right]^2\right]\right] . \quad (3.11)$$

It can readily be verified that the summation occurring above can be expressed in closed form:

$$\sum_{n=0}^{\infty}\frac{1}{n!}n^2y^n=(y+y^2)\exp(y) \quad (3.12)$$

and thus Eq. (3.11) can be rewritten as

$$C_0^{(R)}(|\mathbf{r}_1-\mathbf{r}_2|=s;\beta)\simeq(2\pi\tilde{\beta})^{-1}\exp(-s^2/2\tilde{\beta})\left\{1+\tfrac{1}{3}\left[\frac{s}{2R}\right]^2\left[\frac{2\tilde{\beta}}{s^2}+1-\frac{s^2}{2\tilde{\beta}}\right]+O\left[\left[\frac{s}{2R}\right]^4\right]\right\} , \quad (3.13)$$

where $\tilde{\beta}$ is given by Eq. (3.7).

Equation (3.13) represents the main result of the present investigation. When compared with the "flat" two-dimensional result [4]

$$C_0^{D=2}(s;\beta)=(2\pi\tilde{\beta})^{-1}\exp(-s^2/2\tilde{\beta}) \ , \quad (3.14)$$

we see that the leading term ($R\to\infty$) of $C_0^{(R)}$ coincides with Eq. (3.14). The role of "curvature" is to yield, of course, an R-dependent correction, the term of $O(R^{-2})$ being the leading term.

IV. CALCULATION OF CORRESPONDING DIRAC DENSITY MATRIX

The Dirac density matrix for the system of noninteracting electrons is defined (see, e.g., Ref. [5]) in a parallel way to the canonical density matrix $C(\mathbf{r}_1,\mathbf{r}_2;\beta)$ in Eq. (1.1), namely,

$$\rho(\mathbf{r}_1,\mathbf{r}_2;E)=\sum_j\psi_j(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\Theta(E-\epsilon_j) \ , \quad (4.1)$$

where $\Theta(x)$ denotes the usual unit step function.

Having $C(\mathbf{r}_1,\mathbf{r}_2;\beta)$, one can determine $\rho(\mathbf{r}_1,\mathbf{r}_2;E)$ for the same system by applying an inverse Laplace transform, the two matrices being related by [5]

$$\mathcal{L}_\beta\rho(\mathbf{r}_1,\mathbf{r}_2)=\int_0^\infty dE\,\rho(\mathbf{r}_1,\mathbf{r}_2;E)\exp(-\beta E) =\omega\beta^{-1}C(\mathbf{r}_1,\mathbf{r}_2;\beta) \ , \quad (4.2)$$

where ω is an occupancy factor which is 2 for spin-compensated systems and otherwise unity. Knowledge of the density matrix for free electrons permits one to obtain the kinetic- and exchange-energy densities and is also useful for further density-functional investigations of an interacting electron system in the local-density approximation. This is the motivation then for obtaining the Dirac matrix for the sphere model too.

Applying the relation (4.2) to the canonical density matrix $C_0^{(R)}$ in the form (3.13) and using tables of inverse Laplace transforms [6], we then find for the Dirac matrix of the sphere model:

$$\rho_0^{(R)}\left[|\mathbf{r}_1-\mathbf{r}_2|=s;E=\frac{\hbar^2}{2m_e}k^2\right]\simeq\omega(2\pi s^2)^{-1}\left\{skJ_1(sk)+\frac{2}{3}\left[\frac{s}{2R}\right]^2\left[J_0(sk)+\frac{1}{2}skJ_1(sk)-\frac{1}{4}(sk)^2J_2(sk)\right]+O\left[\left[\frac{s}{2R}\right]^4\right]\right\}, \quad (4.3)$$

where $J_\nu(z)$ is the Bessel function of the first kind. For small $|z|$, this function is given by the series

$$J_\nu(z)=\frac{1}{\Gamma(\nu+1)}\left[\frac{z}{2}\right]^\nu\left[1-\frac{1}{(\nu+1)}\left[\frac{z}{2}\right]^2+O\left[\left[\frac{z}{2}\right]^4\right]\right]. \quad (4.4)$$

We can thus obtain $\rho_0^{(R)}(s;E)$ in the region of small s as

$$\rho_0^{(R)}(s;E)\simeq\frac{\omega}{4\pi}k^2\left\{\left[1-\frac{1}{8}k^2s^2+O(k^4s^4)\right]+\frac{1}{3}\frac{E_R}{E}[1+O(k^4s^4)]+O\left[\left[\frac{E_R}{E}\right]^2\right]\right\}. \quad (4.5)$$

The diagonal element of Eq. (4.5), which is the electron number per unit area, and denoted by $n_0^{(R)}$, can evidently be written as

$$n_0^{(R)}(E)=\rho_0^{(R)}(|\mathbf{r}_1-\mathbf{r}_2|=0;E)\simeq\frac{\omega}{2\pi}\frac{m_eE}{\hbar^2}\left\{1+\frac{1}{3}\frac{E_R}{E}+O\left[\left[\frac{E_R}{E}\right]^2\right]\right\}. \quad (4.6)$$

It should be noted that the expressions (4.3) and (4.6) constitute asymptotic expansions, just as the main result for $C_0^{(R)}$. From Eq. (4.6) it can be seen that the two-term form can yield a good numerical approximation to $n_0^{(R)}(E)$ provided the Fermi energy E of the system satisfies

$$E\gg\tfrac{1}{3}E_R\ . \quad (4.7)$$

This is in agreement with intuition that the Fermi energy must lie in the region of the eigenenergies ϵ_l in Eq. (2.9), with large quantum number l, if the dependence on discrete levels is smeared out in the functions obtained. The result for $n_0^{(R)}$ as a function of E in Eq. (4.6) can be inverted to yield

$$E=\frac{2\pi\hbar^2}{\omega m_e}n_0^{(R)}\left\{1-\frac{1}{3}\frac{\omega}{4\pi R^2n_0^{(R)}}+O\left[\left[\frac{\omega}{4\pi R^2n_0^{(R)}}\right]\right]\right\}. \quad (4.8)$$

When this result is inserted into Eq. (4.3), it yields the density matrix in terms of the particle density $n_0^{(R)}$, thus allowing further density-functional applications.

V. CORRESPONDING CALCULATION OF GREEN FUNCTION

To make contact with the study of Gedik and Ciraci [3], who worked solely with the Green function, let us note next that knowledge of the canonical density matrix $C(\mathbf{r}_1,\mathbf{r}_2;\beta)$ defined in Eq. (1.1) allows one to calculate the Green function. This is taken to be defined as

$$G(\mathbf{r}_1,\mathbf{r}_2;z)=\sum_{\text{all } j}\psi_j(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\frac{1}{z-\epsilon_j} \quad (5.1)$$

for complex energy z. Here, in Eq. (5.1), we take $\epsilon_j\geq 0$ by appropriate choice of a constant in the potential energy.

The relation between C and G is then

$$G(\mathbf{r}_1,\mathbf{r}_2;-E)=-\int_0^\infty d\beta\exp(-\beta E)C(\mathbf{r}_1,\mathbf{r}_2;\beta)=-\mathcal{L}_EC(r_1,r_2)\ , \quad (5.2)$$

where $\mathcal{L}_E$ evidently denotes the Laplace transform, with transformed variable E (>0).

Applying this relation to $C_0^{(R)}$ as given in Eq. (3.13) and using tables of Laplace transforms [6], we find

$$G_0^{(R)}\left[|\mathbf{r}_1-\mathbf{r}_2|=s;-E=\frac{-\hbar^2k^2}{2m_e}\right]\simeq\frac{-m_e}{\pi\hbar^2}\left\{K_0(sk)+\frac{1}{3}\left[\frac{s}{2R}\right]^2\left[\left[\frac{2}{sk}-\frac{sk}{2}\right]K_1(sk)+K_0(sk)\right]+O\left[\left[\frac{s}{2R}\right]^4\right]\right\}, \quad (5.3)$$

where $K_\nu(z)$ denotes the modified Bessel function of the third kind. Knowing the expansions for small $|z|$, namely,

$$K_0(z)=-\ln z+a+\tfrac{1}{4}z^2(-\ln z+a+1)+O(z^4\ln z)\ ,$$
$$K_1(z)=z^{-1}\{1+\tfrac{1}{2}z^2(\ln z-a-\tfrac{1}{2})+O(z^4\ln z)\}\ , \quad (5.4)$$

where $a=\ln 2-\gamma=0.115\,931$, with γ equal to Euler's constant, we can rewrite the Green function $G_0^{(R)}$ for small s^2k^2 as

$$G_0^{(R)}(|\mathbf{r}_1-\mathbf{r}_2|=s;-E)\simeq\frac{-m_e}{\pi\hbar^2}\left\{\left[-\ln(sk)+a+\frac{1}{4}k^2s^2[-\ln(ks)+a+1]+O(k^4s^4\ln(ks))\right]\right.$$
$$\left.+\frac{1}{6}\frac{E_R}{E}\left[1-k^2s^2+O(k^4s^4\ln(ks))\right]+O((E_R/E)^2)\right\}. \qquad (5.5)$$

Noting a similarity between the expansions (5.5) and (4.5), we should reiterate arguments given below Eq. (4.6), leading to the conclusion that the two-term representation (5.3) or (5.5) of the asymptotic series for $G_0^{(R)}(s;E)$ is meaningful for energies E satisfying the inequality (4.7). While Eq. (5.5) is useful for $s^2k^2\ll 1$, i.e., for small s but not too large $E=\hbar^2k^2/2m_e$, the representation (5.3) can be used for arbitrarily large energies E.

This is the point to make explicit contact with the result of Gedik and Ciraci [3]. Their closed-form result, rewritten here in our notation and normalization, reads

$$G_0^{(R)}(s;-E)=\frac{m_e}{2\pi\hbar^2}\left\{\frac{E_R}{-E}+\ln\left[\left(\frac{s}{2R}\right)^2\right]+1+O\left(\frac{E}{E_R}\right)\right\}. \qquad (5.6)$$

This result (5.6) can be derived for energies E satisfying

$$E\ll\epsilon_1=2E_R\ . \qquad (5.7)$$

Therefore the results of Gedik and Ciraci [3] and the present findings are complementary, because they cover different ranges of energy, specified by the inequalities (5.7) and (4.7), respectively, practically "touching" at $E_t=0.8E_R$, where $E_t/2E_R=0.4=\frac{1}{3}E_R/E_t$.

VI. SUMMARY AND FUTURE DIRECTIONS

The main achievement of the present study has been the explicit calculation of the cononical density matrix $C_0^{(R)}(\mathbf{r}_1,\mathbf{r}_2;\beta)$ for free electrons moving on the surface of a sphere of radius R. The result obtained is an asymptotic series in powers of R^{-2}, and Eq. (3.13) exhibits explicitly the first two terms of this expansion, namely, the flat plane result plus the term of $O(R^{-2})$. This result has then been employed to calculate the corresponding Dirac density matrix in Eqs. (4.3) and (4.5), the Fermi energy of the system in Eq. (4.8), and, finally, the Green function given in Eqs. (5.3) and (5.5). The last result is complementary to that obtained by Gedik and Ciraci [3], covering the region of large energies as in Eq. (4.7), while their result is appropriate for small energies as indicated in Eq. (5.7).

As to future work, it is worthy of note that the Green function given by Gedik and Ciraci [3] was employed by them to argue that a pair of electrons moving on the surface of a sphere will bind for an arbitrarily weak (model) attractive interaction. When an understanding of the nature of the attractive interaction in C_{60} is eventually obtained, our results for the same Green function will allow their investigation to be generalized to the case of an attractive interaction of finite strength. Finally, the results given here for the Dirac density matrix offer potential for future density-functional calculations for a system of electrons moving in two-dimensional space having finite curvature.

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APPENDIX: EVALUATION OF $Q_n(\xi^2)$ AS AN ASYMPTOTIC SERIES

To evaluate the function $Q_n(\xi^2)$ defined in Eq. (3.9) it is useful to introduce the variable

$$x=x_l=\xi(l+\tfrac{1}{2})\ . \qquad (A1)$$

In terms of this, one can write various quantities appearing in Eq. (3.9) as

$$\xi^2 l(l+1)=x^2-\tfrac{1}{4}\xi^2 \qquad (A2)$$

and

$$\xi^{2n}\prod_{j=1-n}^{n}(l+j)=\prod_{j=-n+1}^{n}[x+\xi(j-\tfrac{1}{2})]$$
$$=\prod_{j=1}^{n}[x^2-\xi^2(j-\tfrac{1}{2})^2]$$
$$=\sum_{i=0}^{n}t_{ni}\xi^{2i}x^{2(n-i)}\ . \qquad (A3)$$

The coefficients t_{ni} can be deduced from the above product form to be

$$t_{n0}=1\ ,$$
$$t_{n1}=\sum_{j=1}^{n}-(j-\tfrac{1}{2})^2=-\tfrac{1}{12}n(4n^2-1)\ ,$$
$$\vdots \qquad (A4)$$
$$t_{nn}=(-1)^n\prod_{j=1}^{n}(j-\tfrac{1}{2})^2\ .$$

Then, with the help of Eqs. (A1)–(A3), we can rewrite Eq. (3.9) as

$$Q_n(\xi^2)=\frac{2}{n!}\exp(\xi^2/4)\sum_{i=0}^{n}\xi^{2i}t_{ni}T_n[f_{2n+1-2i}]\ , \qquad (A5)$$

where T_n as a function of ξ and a functional of f is given by

$$T_n[f]_\xi=\sum_{l=n}^{\infty}\xi f(\xi(l+\tfrac{1}{2})) \qquad (A6)$$

and

$$f_j(x)=x^j\exp(-x^2)\ ,\quad j=1,3,\ldots\ . \tag{A7}$$

The form of T_n given by Eq. (A6) resembles an integral approximated by discrete summation. Therefore we shall rewrite Eq. (A6), without introducing any approximations as yet, in this spirit:

$$\begin{aligned} T_n[f] &= \int_{n-1/2}^{\infty} f(\xi(\lambda+\tfrac{1}{2}))\xi\,d\lambda+\sum_{l=n}^{\infty}\int_{-1/2}^{1/2}[f(\xi(l+\tfrac{1}{2}))-f(\xi(l+\tfrac{1}{2})+\xi\lambda)]\xi\,d\lambda \\ &= \int_{n\xi}^{\infty} dx\,f(x)-\sum_{k=1}^{\infty}\frac{1}{(2k)!}\xi^{2k}\frac{2}{2k+1}(\tfrac{1}{2})^{2k+1}\left[\sum_{l=n}^{\infty}\xi f^{(2k)}(\xi(l+\tfrac{1}{2}))\right], \end{aligned} \tag{A8}$$

where we have used the notation

$$f^{(m)}(x)=\left[\frac{d}{dx}\right]^m f(x)\ . \tag{A9}$$

To arrive at the form (A8) a change of variable from λ to $x=\xi(\lambda+\frac{1}{2})$ was made in the first integral, while in the second f was expanded in a Taylor series in $(\xi\lambda)$ and then a term-by-term integration over λ was carried out. It is now to be noted that the expression in the square brackets can be written as $T_n[f^{(2k)}]$ according to the definition (A6), so that

$$T_n[f]=\int_{n\xi}^{\infty} dx\,f(x)-\sum_{k_1=1}^{\infty}\frac{1}{(2k_1+1)!}\left[\frac{\xi}{2}\right]^{2k_1}T_n[f^{(2k_1)}]\ . \tag{A10}$$

Equation (A10) can now be iterated many times. Each iteration introduces higher and higher powers of ξ^2 in the series; e.g., after the first iteration we should insert into Eq. (A10) the expression

$$T_n[f^{(2k_1)}]=\int_{n\xi}^{\infty} dx\,f^{(2k_1)}(x)-\sum_{k_2=1}^{\infty}\frac{1}{(2k_2+1)!}\left[\frac{\xi}{2}\right]^{2k_2}\times T_n[f^{(2k_1+2k_2)}]\ , \tag{A11}$$

etc.

Next we evaluate an integral: the leading term in Eq. (A10), for $f(x)=f_{2m+1}(x)$, $m=0,1,2,\ldots$; see Eq. (A7): i.e., a typical function occurring in Eq. (A5):

$$\begin{aligned} \int_{n\xi}^{\infty} dx\,f_{2m+1}(x) &= \left[\int_0^{\infty}-\int_0^{n\xi}\right]dx\,f_{2m+1}(x) \\ &= \int_0^{\infty} dx\,x^{2m+1}\exp(-x^2)-\int_0^{n\xi}dx\sum_{k=0}^{\infty}\frac{(-1)^k}{k!}x^{2k+2m+1} \\ &= \frac{m!}{2}-\xi^{2(m+1)}\sum_{k=0}^{\infty}\frac{(-1)^k n^{2(k+m+1)}}{k!2(k+m+1)}\xi^{2k}\ . \end{aligned} \tag{A12}$$

Again the result obtained is a power series in ξ^2. It is to be noted that the lowest power in this variable is $\xi^{2(m+1)}$.

One can evaluate the leading terms of Eq. (A11) using properties of the functions (A7) to find

$$\begin{aligned} \int_{n\xi}^{\infty} dx\,f_{2m+1}^{(2k)}(x) &= f_{2m+1}^{(2k-1)}(x)\Big|_{x=n\xi}^{x=\infty} \\ &= -f_{2m+1}^{(2k-1)}(n\xi) \\ &= -\left[\left[\frac{d}{dx}\right]^{2k-1}\sum_{j=0}^{\infty}\frac{(-1)^j}{j!}x^{2j+2m+1}\right]_{x=n\xi}, \end{aligned} \tag{A13}$$

which is evidently again a series in ξ^2.

Collecting the results in Eqs. (A10)–(A13) and inserting them into Eq. (A5), we obtain

$$Q_n(\xi^2)\simeq 1+\sum_{i=1}^{\mathcal{N}} q_{ni}\xi^{2i}+O(\xi^{2(\mathcal{N}+1)})\ , \tag{A14}$$

where the coefficients q_{ni} are determined via the procedure outlined above. It needs to be stressed, however, that Eq. (A14) represents an asymptotic expansion. This is so because the function $Q_n(\xi^2)$ is nonanalytic at $\xi^2=0$, which can be seen if we expand formally the function $\xi^{-2(n+1)}Q_n(\xi^2)$ in a power series in ξ^2 using the defining expression (3.9), all coefficients of this formal expansion then being infinite. Due to the properties of the asymptotic expansion, for each fixed ξ_0^2, only a finite number of terms $\mathcal{N}$ gives the best approximation to $Q_n(\xi^2)$ for

$\xi^2 \le \xi_0^2$. This limiting index $\mathcal{N}$ is to be found, roughly speaking, from the condition that the $(\mathcal{N}+1)$th term is larger than its predecessor in absolute value.

It finally remains then to calculate $Q_n(\xi^2)$ up to $O(\xi^2)$ quite explicitly. For $n=0$ we have in Eq. (A5) one term only, so that we need to evaluate

$$T_0[f_1]=\frac{1}{2}-\frac{1}{3!}\left[\frac{\xi}{2}\right]^2 T_0[f_1^{(2)}]_0+O(\xi^4)$$
$$=\frac{1}{2}\left\{1+\frac{\xi^2}{12}+O(\xi^4)\right\} . \quad \text{(A15)}$$

Here we have used Eqs. (A10)–(A13) and the value $f_1^{(1)}(0)=1$. Hence, according to Eq. (A5), we have

$$Q_0(\xi^2)\simeq 2\left\{1+\frac{\xi^2}{4}+O(\xi^4)\right\}\frac{1}{2}\left\{1+\frac{\xi^2}{12}+O(\xi^4)\right\}$$
$$=1+\frac{\xi^2}{3}+O(\xi^4) . \quad \text{(A16)}$$

For $n \ge 1$, within the assumed accuracy, we require only two terms in Eq. (A5), namely, $T_n[f_{2n+1}]$ and $T_n[f_{2n-1}]_0$. Therefore, from Eqs. (A10) and (A12),

$$T_n[f_{2n+1}]=\frac{n!}{2}-\tfrac{1}{24}\xi^2 T_n[f_{2n+1}^{(2)}]_0+O(\xi^4) , \quad \text{(A17)}$$

but $T_n[f_{2n+1}^{(2)}]_0=0$ according to Eqs. (A11) and (A13). Next we have

$$T_n[f_{2n-1}]_0=T_n[f_{2(n-1)+1}]_0$$
$$=\frac{(n-1)!}{2} . \quad \text{(A18)}$$

Therefore, inserting the results (A17) and (A18) and the coefficients t_{n0} and t_{n1}, Eq. (A4), into Eq. (A5), we have finally

$$Q_n(\xi^2)\simeq\frac{2}{n!}\left\{1+\frac{\xi^2}{4}+O(\xi^4)\right\}$$
$$\times\left\{\frac{n!}{2}-\frac{\xi^2}{12}n(4n^2-1)\frac{(n-1)!}{2}\right\}$$
$$=1+\tfrac{1}{3}(1-n^2)\xi^2+O(\xi^4) . \quad \text{(A19)}$$

When compared with Eq. (A16), it can be seen that this result (A19) is valid also for $n=0$.

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