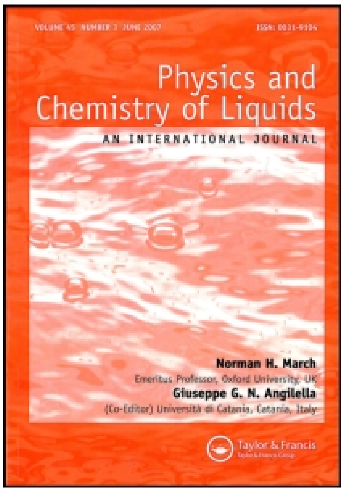

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Generalization to higher dimensions of one-dimensional differential equation for Slater sum of an inhomogeneous electron liquid for a given local potential

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The Slater sum $S(\mathbf{r}, \beta)$ is the diagonal element of the canonical or Bloch density matrix, and by spatial integration yields the partition function. In one dimension, for independent electrons moving in a common potential $v(x)$, the work of March and Murray (*Phys. Rev.*, **120**, 831 (1960)) already yielded a third-order partial differential equation for $S(x, \beta)$. But to date, a generalization to higher dimensions for independent electrons in a given $v(\mathbf{r})$ has not been effected. Here, using the differential virial equation (Holas and March, *Phys. Rev. A*, **51**, 2040 (1995)) such generalization is derived. As a special case, the known differential equation for $S(r, \beta)$ for three-dimensional spherically symmetric harmonic confinement is recovered. This equation is shown to be valid also for a wider, specific class of three-dimensional spherical systems.

Keywords: Inhomogeneous electron liquid; Slater sum; Harmonic confinement

1. Background

In the early work of March and Murray [1], central-field problems in a potential $v(|\mathbf{r}|)$ were analyzed using the canonical or Bloch density matrix. This central-field case is, of course, analogous to a one-dimensional problem. One important result of their work, written now specifically for one-dimensional motion in a common potential energy $v(x)$, was the third-order linear partial differential equation for the Slater sum S, defined by

$$S(x, \beta) = \sum_{j}^{\text{all}} \psi_j(x)\psi_j^*(x)\exp(-\beta\epsilon_j), \quad \beta > 0, \tag{1}$$

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where $\psi_j(x)$ and ϵ_j are respectively the eigenfunctions and eigenvalues generated by the potential $v(x)$. In some applications $\beta = (k_B T)^{-1}$, where k_B is Boltzmann's constant while T is the absolute temperature. The above differential equation then reads

$$\frac{1}{8}\frac{\partial^3 S(x,\beta)}{\partial x^3} = \frac{\partial^2 S(x,\beta)}{\partial x \partial \beta} + v(x)\frac{\partial S(x,\beta)}{\partial x} + \frac{1}{2}\frac{\mathrm{d}v(x)}{\mathrm{d}x} S(x,\beta) \tag{2}$$

(atomic units are used throughout this article).

2. Differential virial equation in terms of density and density matrix

In an attempt to generalize equation (2) to higher dimensions, we next invoke the so-called differential virial equation derived by Holas and March [2]. If we consider a noninteracting many-electron system moving in a general one-body potential $v(\mathbf{r})$, for arbitrary dimensionality of the space $D = 1, 2, \ldots,$ we have

$$-n(\mathbf{r}, E)\nabla v(\mathbf{r}) = \mathbf{z}(\mathbf{r}, E) - \frac{1}{4}\nabla\nabla^2 n(\mathbf{r}, E). \tag{3a}$$

Here, the kinetic vector

$$\mathbf{z}(\mathbf{r}, E) = \hat{\mathbf{O}}(\mathbf{r}', \mathbf{r}'')\rho(\mathbf{r}+\mathbf{r}'; \mathbf{r}+\mathbf{r}'', E)|_{\mathbf{r}'=\mathbf{r}''=\mathbf{0}}, \tag{3b}$$

represents a combination of derivatives of the kinetic energy density tensor, so it can be written as a vector differential operator $\hat{\mathbf{O}}$ acting on the Dirac density matrix

$$\rho(\mathbf{r}_1; \mathbf{r}_2, E) = \sum_j^{\text{all}} \Theta(E - \epsilon_j)\psi_j(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2), \tag{4}$$

where Θ is the unit step function, $\Theta(\xi) = 1$ for $\xi \geq 0$, $\Theta(\xi) = 0$ for $\xi < 0$. The particle-number density is given as the diagonal of the matrix ρ:

$$n(\mathbf{r}, E) = \rho(\mathbf{r};\, \mathbf{r}, E). \tag{5}$$

The normalized orbitals $\psi_j(\mathbf{r})$ and orbital energies ϵ_j are eigensolutions of the one-electron Schrödinger equation

$$\big(\hat{t}(\mathbf{r}) + v(\mathbf{r})\big)\psi_j(\mathbf{r}) = \epsilon_j \psi_j(\mathbf{r}), \tag{6a}$$

$$\hat{t}(\mathbf{r}) = -\frac{1}{2}\nabla^2(\mathbf{r}) = -\frac{1}{2}\sum_{\mu=1}^{D}(\partial/\partial r_\mu)^2. \tag{6b}$$

The spin coordinate of the orbital is included to the label j. A constant such that $\epsilon_j > 0\ \forall\, j$ is added to $v(\mathbf{r})$.

The α component of the differential operator $\hat{\mathbf{O}}$ [for construction of the kinetic vector $\mathbf{z}$, equation (3b)] is defined as

$$\hat{O}_\alpha(\mathbf{r}', \mathbf{r}'') = \frac{1}{2}\sum_{\beta=1}^{D}\left(\frac{\partial}{\partial r'_\beta} + \frac{\partial}{\partial r''_\beta}\right)\left(\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta} + \frac{\partial^2}{\partial r'_\beta \partial r''_\alpha}\right), \quad \alpha = 1, 2, \ldots, D \tag{7}$$

(see Holas and March [2]). In the case when $\hat{\mathbf{O}}$ is acting on a real, symmetric matrix [e.g., when ρ, equation (4), is constructed of *real* orbitals only], this operator simplifies to

$$\hat{O}_\alpha(\mathbf{r}', \mathbf{r}'') = \sum_{\beta=1}^{D}\left(\frac{\partial}{\partial r'_\beta} + \frac{\partial}{\partial r''_\beta}\right)\frac{\partial^2}{\partial r'_\alpha \partial r''_\beta}. \tag{8}$$

3. Differential virial equation in terms of Slater sum and canonical density matrix

The Dirac density matrix $\rho(\mathbf{r}_1; \mathbf{r}_2, E)$, equation (4), is related to the canonical density matrix

$$C(\mathbf{r}_1;\, \mathbf{r}_2, \beta) = \sum_{j}^{\text{all}} \psi_j(\mathbf{r}_1)\psi_j^*(\mathbf{r}_2)\exp(-\beta\epsilon_j), \quad \beta > 0, \tag{9}$$

by the Laplace transform (March and Murray [1])

$$\beta^{-1}C(\mathbf{r}_1;\, \mathbf{r}_2, \beta) = \int_0^\infty \mathrm{d}E\, \rho(\mathbf{r}_1;\, \mathbf{r}_2, E)\exp(-\beta E), \tag{10}$$

and this transform relates also the density $n(\mathbf{r}, E)$, equation (5), to the diagonal of C — the canonical particle-number density (called the Slater sum, the object of our interest)

$$S(\mathbf{r}, \beta) = C(\mathbf{r};\, \mathbf{r}, \beta). \tag{11}$$

The canonical density matrix, equation (9), satisfies the Bloch equation [3]

$$\big(\hat{t}(\mathbf{r}_1) + v(\mathbf{r}_1)\big)C(\mathbf{r}_1;\, \mathbf{r}_2, \beta) = -\frac{\partial C(\mathbf{r}_1;\, \mathbf{r}_2, \beta)}{\partial \beta}. \tag{12}$$

By inserting $\mathbf{r}_1 = \mathbf{r}_2 = \mathbf{r}$, the β derivative of the Slater sum is obtained

$$\frac{\partial S(\mathbf{r}, \beta)}{\partial \beta} = -k(\mathbf{r}, \beta) - v(\mathbf{r})\, S(\mathbf{r}, \beta), \tag{13a}$$

where the canonical kinetic energy density is

$$k(\mathbf{r},\beta)=\frac{1}{2}\big(\hat{t}(\mathbf{r}')+\hat{t}(\mathbf{r}'')\big)C(\mathbf{r}+\mathbf{r}';\ \mathbf{r}+\mathbf{r}'',\beta)|_{\mathbf{r}'=\mathbf{r}''=\mathbf{0}} \tag{13b}$$

(this symmetric expression is an average of two equivalent forms).

After applying the Laplace transform to both sides of equation (3a), we obtain immediately the sought for differential equation for the Slater-sum function

$$-S(\mathbf{r},\beta)\nabla v(\mathbf{r})=\mathbf{Z}(\mathbf{r},\beta)-\frac{1}{4}\nabla\nabla^2 S(\mathbf{r},\beta), \tag{14a}$$

where the canonical kinetic vector

$$\mathbf{Z}(\mathbf{r},\beta)=\hat{\mathbf{O}}(\mathbf{r}',\mathbf{r}'')C(\mathbf{r}+\mathbf{r}';\ \mathbf{r}+\mathbf{r}'',\beta)|_{\mathbf{r}'=\mathbf{r}''=\mathbf{0}}, \tag{14b}$$

is, in fact, the Laplace transform of the kinetic vector $\mathbf{z}(\mathbf{r},E)$, equation (3b). Equation (14) represents the main result of our article.

4. Proof of generalization

To see that equation (14) is really a generalization to higher dimensions of the one-dimensional equation (2), let us rewrite this equation (14) for $D=1$, reducing $\mathbf{r}$ to x:

$$-S(x,\beta)\frac{\mathrm{d}v(x)}{\mathrm{d}x}=Z(x,\beta)-\frac{1}{4}\frac{\partial^3 S(x,\beta)}{\partial x^3}, \tag{15a}$$

where, according to equations (14b) and (7),

$$Z(x,\beta)=\left(\frac{\partial}{\partial x'}+\frac{\partial}{\partial x''}\right)\frac{\partial^2}{\partial x'\partial x''}C(x+x';x+x'',\beta)|_{x'=x''=0}. \tag{15b}$$

To make equation (2) comparable with equation (15a), we substitute for $\partial S(x,\beta)/\partial\beta$ the expression given in equation (13a) and obtain, after a simple algebra,

$$-S(x,\beta)\frac{\mathrm{d}v(x)}{\mathrm{d}x}=\tilde{Z}(x,\beta)-\frac{1}{4}\frac{\partial^3 S(x,\beta)}{\partial x^3}, \tag{16a}$$

where

$$\tilde{Z}(x,\beta)=\frac{\partial}{\partial x}\left(2\,k(x,\beta)+\frac{1}{2}\frac{\partial^2 S(x,\beta)}{\partial x^2}\right). \tag{16b}$$

With the help of equations (13b) and (11), this $\tilde{Z}$ can be rewritten as

$$\tilde{Z}(x,\beta) = \frac{1}{2}\frac{\partial}{\partial x}\left(-\left(\frac{\partial}{\partial x'}\right)^2 - \left(\frac{\partial}{\partial x''}\right)^2 + \left(\frac{\partial}{\partial x}\right)^2\right) C(x+x'; x+x'', \beta)|_{x'=x''=x}. \quad (17)$$

After replacing $\partial/\partial x$ by $(\partial/\partial x' + \partial/\partial x'')$, we arrive at

$$\tilde{Z}(x,\beta) = \hat{\tilde{o}}(x', x'')\, C(x+x'; x+x'', \beta)|_{x'=x''=0}, \quad (18a)$$

where

$$\begin{aligned}\hat{\tilde{o}}(x', x'') &= \frac{1}{2}\left(\frac{\partial}{\partial x'} + \frac{\partial}{\partial x''}\right)\left(-\left(\frac{\partial}{\partial x'}\right)^2 - \left(\frac{\partial}{\partial x''}\right)^2 + \left(\frac{\partial}{\partial x'} + \frac{\partial}{\partial x''}\right)^2\right)\\ &= \frac{1}{2}\left(\frac{\partial}{\partial x'} + \frac{\partial}{\partial x''}\right)\left(2\,\frac{\partial}{\partial x'}\frac{\partial}{\partial x''}\right).\end{aligned} \quad (18b)$$

Thus $\tilde{Z}(x,\beta)$, equation (18), coincides with $Z(x,\beta)$, equation (15b). This ends the proof that our generalization, equation (14), taken for $D=1$ is equivalent to the early result derived by March and Murray [1] for $D=1$, equation (2). Although equation (2) involves only two functions — the system potential v and the Slater sum S — together with their derivatives (including the derivative of S with respect to β), it can be rewritten in a form where the β derivative is eliminated, but at the cost of involving spatial derivatives of the canonical density matrix C [taken at its diagonal, see equation (18)]. The generalization to higher dimensions repeats this last form, i.e., it involves both S and C, equation (14).

5. Example of three-dimensional isotropic harmonic oscillator

For the system of independent electrons in $D=3$ moving in the isotropic harmonic (IH) confinement

$$v(\mathbf{r}) = v(r,\omega) = \frac{1}{2}\omega^2 r^2 \quad (19)$$

(the constant ω^2 controls its strength), the canonical density matrix is known (Sondheimer and Wilson [4])

$$C(\mathbf{r}_1; \mathbf{r}_2, \beta, \omega) = N(\beta,\omega)\exp\left(-\omega A(\beta\omega)\left(\frac{\mathbf{r}_1+\mathbf{r}_2}{2}\right)^2 - \omega B(\beta\omega)\left(\frac{\mathbf{r}_1-\mathbf{r}_2}{2}\right)^2\right), \quad (20a)$$

where

$$N(\beta,\omega) = \left(\frac{\omega}{2\pi\sinh(\beta\omega)}\right)^{3/2}, \quad A(\beta\omega) = \tanh(\beta\omega/2), \quad B(\beta\omega) = 1/A(\beta\omega). \quad (20b)$$

The Slater sum, equation (11), follows from it in the form

$$S(r,\beta,\omega) = N(\beta,\omega)\exp\bigl(-\omega A(\beta\omega)\, r^2\bigr). \tag{21}$$

We are going to verify that the above written canonical density matrix C and the Slater sum S satisfy our equation (14). Due to the isotropy of the system, this vector equation reduces to one equation for the radial component (formally, after multiplying equation (14) by $\partial\mathbf{r}/\partial r$, i.e., $\mathbf{r}/r$)

$$-S(r,\beta,\omega)\frac{\partial v(r,\omega)}{\partial r} = Z_{\text{rad}}(r,\beta,\omega) - \frac{1}{4}\frac{\partial}{\partial r}\boldsymbol{\nabla}^2 S(r,\beta,\omega), \tag{22a}$$

where the radial component of the canonical kinetic vector is

$$Z_{\text{rad}}(r,\beta,\omega) = \sum_{\alpha}\frac{r_\alpha}{r}\, Z_\alpha(\mathbf{r},\beta,\omega). \tag{22b}$$

It can be evaluated immediately using results obtained in Appendix A. By comparing equation (20a) with equations (A4) and (A3) we find for the IH confinement

$$\tilde{C}(\xi_1,\xi_2,\xi_3,\beta,\omega) = N(\beta,\omega)\exp\bigl(-\omega A(\beta\omega)\xi_1 - \omega B(\beta\omega)\xi_2\bigr) \tag{23}$$

(here $\tilde{C}$ happens to be independent of ξ_3). The 2nd- and 3rd-order derivatives of $\tilde{C}$, which occur in equation (A8), are evaluated according to equation (A9) applied to equation (23). The results are

$$\tilde{C}_{200} = (\omega A)^2 S, \qquad \tilde{C}_{110} = \omega A\,\omega B S = \omega^2 S, \tag{24a}$$

$$\tilde{C}_{300} = -(\omega A)^3 S, \qquad \tilde{C}_{ijl} = 0 \quad \text{for} \ \ 1 \neq 0. \tag{24b}$$

After inserting them into equation (A8) we obtain finally

$$Z_{\text{rad}}(r,\beta,\omega) = \bigl[5(\omega A)^2 r - \omega^2 r - 2(\omega A)^3 r^3\bigr] S(r,\beta,\omega). \tag{25}$$

Due to the spherical symmetry of S, the term involving its Laplacian

$$\boldsymbol{\nabla}^2 S(r,\beta,\omega) = \left[\left(\frac{\partial}{\partial r}\right)^2 + \frac{2}{r}\frac{\partial}{\partial r}\right] S(r,\beta,\omega) \tag{26a}$$

in equation (22a) is

$$\frac{\partial}{\partial r}\boldsymbol{\nabla}^2 S(r,\beta,\omega) = \left[\left(\frac{\partial}{\partial r}\right)^3 + \frac{2}{r}\left(\frac{\partial}{\partial r}\right)^2 - \frac{2}{r^2}\frac{\partial}{\partial r}\right] S(r,\beta,\omega). \tag{26b}$$

Differentiation of S, which is given in equation (21), gives

$$\frac{\partial S}{\partial r} = -2\omega A r S, \quad \frac{\partial^2 S}{\partial r^2} = \left(-2\omega A + (2\omega A r)^2\right)S, \quad \frac{\partial^3 S}{\partial r^3} = \left(3(2\omega A)^2 - (2\omega A r)^3\right)S. \qquad (27)$$

So

$$-\frac{1}{4}\frac{\partial}{\partial r}\nabla^2 S(r,\beta,\omega) = \left[-5(\omega A)^2 r + 2(\omega A)^3 r^3\right]S(r,\beta,\omega). \qquad (28)$$

By noting that the derivative of the IH potential, equation (19), is $\partial v(r,\omega)/\partial r = \omega^2 r$, we see that the sum of equations (25) and (28) equals $-S\partial v/\partial r$, so equation (22a) is really satisfied.

Amovilli and March [5] derived the following partial differential equation for the Slater sum of the considered system:

$$\left[\frac{1}{8}\left(\frac{\partial}{\partial r}\right)^3 + \frac{1}{4r}\left(\frac{\partial}{\partial r}\right)^2 - \left(\frac{1}{4r^2} + v(r,\omega) + \frac{\partial}{\partial \beta}\right)\frac{\partial}{\partial r} + \frac{1}{2}\frac{\partial v(r,\omega)}{\partial r}\right]S(r,\beta,\omega) = 0. \qquad (29)$$

With the help of equation (26) it can be rewritten as

$$\frac{1}{8}\frac{\partial}{\partial r}\nabla^2 S(r,\beta,\omega) - \left(v(r,\omega) + \frac{\partial}{\partial \beta}\right)\frac{\partial S(r,\beta,\omega)}{\partial r} + \frac{1}{2}\frac{\partial v(r,\omega)}{\partial r}S(r,\beta,\omega) = 0. \qquad (30)$$

After eliminating $\partial S/\partial \beta$ with the help of equation (13a) and some simple algebra the following equation is obtained

$$-S(r,\beta,\omega)\frac{\partial v(r,\omega)}{\partial r} = \frac{\partial}{\partial r}\left(\frac{2}{3}k(r,\beta,\omega) + \frac{1}{3}\nabla^2 S(r,\beta,\omega)\right) - \frac{1}{4}\frac{\partial}{\partial r}\nabla^2 S(r,\beta,\omega). \qquad (31)$$

This radial equation for the Slater sum in terms of r is quite similar to the one-dimensional equation in terms of x, equation (16). When compared with equation (22a), we see that

$$Z_{\text{rad}}^{\text{alt}}(r,\beta,\omega) = \frac{\partial}{\partial r}\left(\frac{2}{3}k(r,\beta,\omega) + \frac{1}{3}\nabla^2 S(r,\beta,\omega)\right), \qquad (32)$$

plays the role of an alternative expression for the radial component of the canonical kinetic vector. The coefficients in the expression for $Z_{\text{rad}}^{\text{alt}}(r,\beta,\omega)$ are different than in its one-dimensional analogue $\tilde{Z}(x,\beta)$, equation (16b).

To evaluate $Z_{\text{rad}}^{\text{alt}}$, let us differentiate $k(r,\beta,\omega)$ from equation (A10), remembering that in the present system $\tilde{C}_{ijl} = 0$ for $l \neq 0$, and that arguments of $\tilde{C}_{ijl}$ are given in equation (A9b):

$$\frac{\partial k(r,\beta,\omega)}{\partial r} = \frac{\partial}{\partial r}\left[-\frac{3}{4}(\tilde{C}_{100} + \tilde{C}_{010}) - \frac{1}{2}\tilde{C}_{200}r^2\right] = -\frac{5}{2}\tilde{C}_{200} - \frac{3}{2}\tilde{C}_{110} - \tilde{C}_{300}r^2. \qquad (33)$$

Having this result for $\partial k/\partial r$ [with the values of $\tilde{C}_{ijl}$ taken from equation (24)], and equation (28) for the Laplacian term, we obtain from equation (32) the final expression for the alternative radial component of the kinetic vector

$$\begin{aligned} Z_{\mathrm{rad}}^{\mathrm{alt}}(r,\beta,\omega) &= \frac{2}{3}\left[-\frac{5}{2}(\omega A)^2 r - \frac{3}{2}\omega^2 r + (\omega A)^3 r^3\right]S - \frac{4}{3}\left[-5(\omega A)^2 r + 2(\omega A)^3 r^3\right]S \\ &= \left[5(\omega A)^2 r - \omega^2 r - 2(\omega A)^3 r^3\right]S(r,\beta,\omega). \end{aligned} \tag{34}$$

As we see, this expression, obtained from $S(r,\beta,\omega)$ by means of differentiations (including also $\partial/\partial\beta$) is exactly the same as the radial component of the kinetic vector $Z_{\mathrm{rad}}(r,\beta,\omega)$, equation (25), obtained from the Bloch matrix $C(\mathbf{r}_1;\mathbf{r}_2,\beta,\omega)$ by means of differentiations. Thus the Amovilli–March [5] partial differential equation for the Slater sum of the IH system, equation (29), is equivalent to the the radial component, equation (22a), of our generalization, equation (14a), at D=3.

6. Other three-dimensional isotropic systems

It would be interesting to check if the Amovilli–March [5] partial differential equation for the Slater sum obtained specifically for the IH system, equation (29), is valid for other isotropic systems. For that reason we should evaluate $Z_{\mathrm{rad}}^{\mathrm{alt}}(r,\beta,\omega)$, equation (32) and $Z_{\mathrm{rad}}(r,\beta,\omega)$, equation (22b), both for a general isotropic system and compare them.

The results obtained in the Appendix A, equations (A10) and (A11), applied directly to $Z_{\mathrm{rad}}^{\mathrm{alt}}(r,\beta,\omega)$, equation (32), yield

$$\begin{aligned} Z_{\mathrm{rad}}^{\mathrm{alt}}(r,\beta,\omega) &= \frac{\partial}{\partial r}\left\{\frac{2}{3}\left(-\frac{1}{2}\right)\left[\frac{3}{2}(\tilde{C}_{100}+\tilde{C}_{010}) + (\tilde{C}_{200}+2\tilde{C}_{001})r^2\right] + \frac{1}{3}\left[6\tilde{C}_{100}+4\tilde{C}_{200}r^2\right]\right\} \\ &= \frac{\partial}{\partial r}\left[\frac{3}{2}\tilde{C}_{100} - \frac{1}{2}\tilde{C}_{010} + \left(\tilde{C}_{200} - \frac{2}{3}\tilde{C}_{001}\right)r^2\right] \\ &= \left(5\tilde{C}_{200} - \tilde{C}_{110} - \frac{4}{3}\tilde{C}_{001}\right)r + \left(2\tilde{C}_{300} - \frac{4}{3}\tilde{C}_{101}\right)r^3. \end{aligned} \tag{35}$$

Let us compare this result (35) with $Z_{\mathrm{rad}}(r,\beta,\omega)$ given in equation (A8). The coefficients at $\tilde{C}_{200}$, $\tilde{C}_{110}$, and $\tilde{C}_{300}$, are the same, while those at $\tilde{C}_{001}$ and $\tilde{C}_{101}$ are different. This means that the Amovilli–March [5] partial differential equation for the Slater sum, equation (29), is not valid for a general isotropic system. However, it is valid for specific isotropic systems having the canonical density matrix in the form

$$C(\mathbf{r}_1;\,\mathbf{r}_2,\beta) = \tilde{C}\big(\xi_1(\mathbf{r}_1,\mathbf{r}_2),\xi_2(\mathbf{r}_1,\mathbf{r}_2),\beta\big) \tag{36}$$

[see equation (A3) for ξ_a]. It differs from C for a general isotropic system, equation (A4), by being independent of $\xi_3(\mathbf{r}_1,\mathbf{r}_2)$ (therefore resulting in $\tilde{C}_{ij1}=0$), however, the form of its dependence on ξ_1 and ξ_2 remains arbitrary. In the case of the IH system — an example of this specific isotropic system — that dependence is exponential, equation (20a).

7. Conclusions

Equation (14) — our main result — represents generalization to higher dimensions of the March–Murray [1] one-dimensional differential equation for the Slater sum, equation (2). For isotropic systems, this vector equation (14) reduces to the radial-component equation (22). The Amovilli–March [5] differential equation for the Slater sum of the isotropic harmonic-potential system, equation (29), is shown to be valid also for a wider class of isotropic three-dimensional systems having the canonical density matrix in the form (36).

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Appendix A: Canonical kinetic vector and kinetic energy density for spherical systems

For spherical (isotropic) systems, characterized by $v(\mathbf{r}) = v(|\mathbf{r}|)$, the eigensolution of the one-electron equation (6) can be written in the form [6] $\{\epsilon_{ln}, \psi_{lnm}(\mathbf{r})\}$, labeled with the orbital quantum number (QN) $l = 0, 1, \ldots,$ the magnetic QN $m = -l, (-l+1), \ldots, l$, and the radial QN $n = 0, 1, \ldots,$ where

$$\psi_{lnm}(\mathbf{r}) = r^{-1}\chi_{ln}(r)\,Y_{lm}(\hat{\mathbf{r}}), \quad r = |\mathbf{r}|, \quad \hat{\mathbf{r}} = \mathbf{r}/r, \tag{A1}$$

with $\chi_{ln}(r)$ being the real eigenfunction of the radial Schrödinger equation, and $Y_{lm}(\hat{\mathbf{r}})$ — the spherical harmonic function. The Dirac matrix, equation (4), for this system is therefore

$$\rho(\mathbf{r}_1; \mathbf{r}_2, E) = \sum_{l=0}^{\infty} R_l(r_1; r_2, E)\,P_l(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2), \tag{A2a}$$

where, including the spin degeneration,

$$R_l(r_1; r_2, E) = 2\sum_n \Theta(E - \epsilon_{ln})\,r_1^{-1}\chi_{ln}(r_1)\,r_2^{-1}\chi_{ln}(r_2)(2l+1)/(4\pi) = R_l(r_2; r_1, E), \tag{A2b}$$

and $P_l(\zeta)$ is the Legandre polynomial, because it satisfies the identity

$$\sum_{m=-l}^{l} Y_{lm}(\hat{\mathbf{r}}_1)\,Y^*_{lm}(\hat{\mathbf{r}}_2) = \frac{2l+1}{4\pi}P_l(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2). \tag{A2c}$$

As we see, the Dirac matrix ρ, equation (A2a), depends on three scalar variables r_1, r_2, and $\zeta = \hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2$ — three invariants constructed of two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. This matrix is symmetric in $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$ and real. The canonical density matrix $C(\mathbf{r}_1; \mathbf{r}_2, \beta)$, equation (9), being the Laplace transform of $\rho(\mathbf{r}_1; \mathbf{r}_2, E)$, equation (10), shows the same properties.

Therefore, the simplified form of the differential operator $\hat{O}_\alpha(\mathbf{r}', \mathbf{r}'')$, equation (8), acting on C can be applied.

It will be convenient to consider C to be a function of three other invariants, namely

$$\xi_1(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{\mathbf{r}_1 + \mathbf{r}_2}{2}\right)^2 = \frac{1}{4}\left[r_1^2 + r_2^2 + 2r_1 r_2 \zeta\right], \tag{A3a}$$

$$\xi_2(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{\mathbf{r}_1 - \mathbf{r}_2}{2}\right)^2 = \frac{1}{4}\left[r_1^2 + r_2^2 - 2r_1 r_2 \zeta\right], \tag{A3b}$$

$$\eta(\mathbf{r}_1, \mathbf{r}_2) = \frac{\mathbf{r}_1^2 - \mathbf{r}_2^2}{2} = \frac{r_1^2 - r_2^2}{2}. \tag{A3c}$$

The constraint

$$\eta^2 \le 4\xi_1 \xi_2 \tag{A3d}$$

should be imposed in order to have $(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{r}}_2)^2 \le 1$ satisfied. The set $\{\xi_1, \xi_2, \eta\}$ of invariants is equivalent to the original set $\{r_1, r_2, \zeta\}$ because, besides the transformation $\{r_1, r_2, \zeta\} \to \{\xi_1, \xi_2, \eta\}$, shown above, a reciprocal transformation is possible: $r_1 = (\xi_1 + \xi_2 + \eta)^{1/2}$, $r_2 = (\xi_1 + \xi_2 - \eta)^{1/2}$, $\zeta = (\xi_1 - \xi_2)\big((\xi_1 + \xi_2)^2 - \eta^2\big)^{-1/2}$. While ξ_1 and ξ_2 are symmetric in $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, η is antisymmetric. Therefore C should depend on

$$\xi_3(\mathbf{r}_1, \mathbf{r}_2) = \eta^2(\mathbf{r}_1, \mathbf{r}_2) = \left[\frac{(\mathbf{r}_1 - \mathbf{r}_2)(\mathbf{r}_1 + \mathbf{r}_2)}{2}\right]^2 \tag{A3e}$$

rather than on η to preserve the symmetry:

$$C(\mathbf{r}_1; \mathbf{r}_2, \beta) = \tilde{C}(\xi_1, \xi_2, \xi_3, \beta). \tag{A4}$$

In terms of $\tilde{C}$, the Slater sum is

$$S(\mathbf{r}, \beta) = C(\mathbf{r}; \mathbf{r}, \beta) = \tilde{C}(r^2, 0, 0, \beta) = S(r, \beta). \tag{A5}$$

When evaluating $k(\mathbf{r}, \beta)$, equation (13b) with (6b), or $Z_\alpha(\mathbf{r}, \beta)$, equation (14b) with (8), the chain-rule differentiation of C is applied, e.g.,

$$\frac{\partial}{\partial r'_\alpha} C(\mathbf{r} + \mathbf{r}'; \mathbf{r} + \mathbf{r}'', \beta) = \sum_{a=1}^{3} \frac{\partial \tilde{C}(\xi_1, \xi_2, \xi_3, \beta)}{\partial \xi_a} \frac{\partial \xi_a(\mathbf{r} + \mathbf{r}', \mathbf{r} + \mathbf{r}'')}{\partial r'_\alpha}. \tag{A6}$$

According to equation (A3) in the three-dimensional space, the functions $\xi_a(\mathbf{r} + \mathbf{r}', \mathbf{r} + \mathbf{r}'')$, $a = 1, 2, 3$, which occur in equation (A6), are

$$\xi_1, \xi_2, \xi_3 = \sum_{\mu=1}^{3} \frac{1}{4}(2r_\mu + r'_\mu + r''_\mu)^2, \quad \sum_{\mu=1}^{3} \frac{1}{4}(r'_\mu - r''_\mu)^2, \quad \frac{1}{4}\left(\sum_{\mu=1}^{3}(r'_\mu - r''_\mu)(2r_\mu + r'_\mu + r''_\mu)\right)^2. \tag{A7}$$

Second and third derivatives of C are evaluated similarly.

After all differentiations and a tedious but straightforward algebra, the following result is obtained for the radial component of the canonical kinetic vector, equation (22b),

$$Z_{\mathrm{rad}}(r,\beta,\omega) = (5\tilde{C}_{200} - \tilde{C}_{110} - 8\tilde{C}_{001})r + (2\tilde{C}_{300} - 4\tilde{C}_{101})r^3, \tag{A8}$$

where

$$\tilde{C}_{ijl} = \left.\frac{\partial^{i+j+l}\tilde{C}(\xi_1,\xi_2,\xi_3,\beta)}{(\partial\xi_1)^i(\partial\xi_2)^j(\partial\xi_3)^l}\right|_0, \tag{A9a}$$

taken at $\mathbf{r}' = \mathbf{r}'' = \mathbf{0}$, i.e., at

$$(\xi_1,\xi_2,\xi_3,\beta) = (r^2,0,0,\beta). \tag{A9b}$$

The kinetic energy density $k(\mathbf{r},\beta)$, equation (13b), for isotropic systems can be also evaluated using the same methods. The result is

$$k(r,\beta) = -\frac{1}{2}\left[\frac{3}{2}(\tilde{C}_{100} + \tilde{C}_{010}) + (\tilde{C}_{200} + 2\tilde{C}_{001})r^2\right]. \tag{A10}$$

Finally, evaluation of the Laplacian of S, equation (26a), for S given in equation (A5), results in

$$\nabla^2 S(r,\beta) = 6\tilde{C}_{100} + 4\tilde{C}_{200}r^2. \tag{A11}$$

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