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Direct solution of the H(1s)–H$^+$ long-range interaction problem in momentum space

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Perturbation equations for the H(1s)–H$^+$ long-range interaction are solved directly in momentum space up to the fourth order with respect to the reciprocal of the internuclear distance. As in the hydrogen atom problem, the Fock transformation is used which projects the momentum vector of an electron from the three-dimensional hyperplane onto the four-dimensional hypersphere. Solutions are given as linear combinations of several four-dimensional spherical harmonics. The present results add an example to the momentum-space solution of the nonspherical potential problem.

I. INTRODUCTION

In a recent paper,[1] the long-range interaction between the ground-state hydrogen atom and the proton has been studied from the momentum-space viewpoint, and it has been shown that the origin of the stabilization $\Delta E = -(9/4)R^{-4} + O(R^{-6})$ of this system is interpretable as the contractive reorganization of the momentum density. In that study, the required perturbation wave function in the momentum representation has been derived by the Dirac–Fourier transformation of the corresponding wave function in the position representation, which is analytically known as a power series of the reciprocal of the internuclear distance R by the long-range perturbation theory.[2]

In this paper, we show that the perturbation equation for the H(1s)–H$^+$ long-range interaction problem can be directly solved in momentum space. The kernel of the integral equation is expanded by the four-dimensional spherical harmonics after the Fock transformation[3-5] which projects the momentum vector of an electron from the three-dimensional hyperplane onto the four-dimensional hypersphere. Then the integral perturbation equation in momentum space is solved up to the fourth order (with respect to R^{-1}) based on the orthonormal property of the four-dimensional spherical harmonics. Solutions are given as linear combinations of these harmonics, and are identical with the previous results[1] obtained by the Dirac–Fourier transformation of the solutions of the position-space perturbation equation[2] when the inverse Fock transformation is carried out. The present results add an example to the exact solution of momentum-space Schrödinger equations. Atomic units are used throughout this paper.

II. THEORETICAL GROUND

A. Perturbation equation in momentum space

The momentum-space Schrödinger equation for a one-electron system is given by

$$[p^2/2 - E]\Psi(\mathbf{p}) + \int U(\mathbf{q})\Psi(\mathbf{p}-\mathbf{q})d\mathbf{q} = 0, \tag{1a}$$

$$U(\mathbf{q}) = (2\pi)^{-3}\int \exp(-i\mathbf{q}\mathbf{r})V(\mathbf{r})d\mathbf{r}, \tag{1b}$$

where $V(\mathbf{r})$ is the potential energy operator in the position representation. For the present system of H(1s)–H$^+$ long-range interaction, $V(\mathbf{r})$ is

$$V(\mathbf{r}) = V_0(\mathbf{r}) + V'(\mathbf{r}), \tag{2a}$$

$$V_0(\mathbf{r}) = -r^{-1}, \quad r = |\mathbf{r}|, \tag{2b}$$

$$V'(\mathbf{r}) = -r'^{-1} + R^{-1} = \sum_{n=1}^{\infty} R^{-(n+1)}V_n(\mathbf{r}), \tag{2c}$$

$$V_n(\mathbf{r}) = -r^nP_n(\cos\theta_r). \tag{2d}$$

Equations (2c) and (2d) follow from the Legendre expansion of the reciprocal of the electron–proton distance r', and θ_r denotes the angle of $\mathbf{r}$ measured from the internuclear axis. Then the momentum-space counterparts

$$U(\mathbf{q}) = U_0(\mathbf{q}) + \sum_{n=1}^{\infty} R^{-(n+1)}U_n(\mathbf{q}), \tag{3a}$$

$$U_n(\mathbf{q}) = (2\pi)^{-3}\int \exp(-i\mathbf{q}\mathbf{r})V_n(\mathbf{r})d\mathbf{r}, \quad n = 0, 1, 2, \cdots \tag{3b}$$

are found to be

$$U_0(\mathbf{q}) = -(2\pi^2)^{-1}q^{-2}, \quad q = |\mathbf{q}|, \tag{3c}$$

$$U_1(\mathbf{q}) = (-i)\delta^{(0,0,1)}(\mathbf{q}), \tag{3d}$$

$$U_2(\mathbf{q}) = -(1/2)[\delta^{(2,0,0)}(\mathbf{q}) + \delta^{(0,2,0)}(\mathbf{q}) - 2\delta^{(0,0,2)}(\mathbf{q})], \tag{3e}$$

$$U_3(\mathbf{q}) = -(i/2)[3\delta^{(2,0,1)}(\mathbf{q}) + 3\delta^{(0,2,1)}(\mathbf{q}) - 2\delta^{(0,0,3)}(\mathbf{q})], \tag{3f}$$

and so on, where $\delta^{(l,m,n)}(\mathbf{q})$ represents the product $[d^l\delta(q_x)/dq_x^l][d^m\delta(q_y)/dq_y^m][d^n\delta(q_z)/dq_z^n]$.

If we assume the expansions

$$E = \sum_{n=0}^{\infty} R^{-n}E_n, \tag{4a}$$

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$$\Psi(\mathbf{p}) = \sum_{n=0}^{\infty} R^{-n}\psi_n(\mathbf{p}), \tag{4b}$$

and equate to zero the coefficients of the individual powers of R^{-1} of Eq. (1a), we obtain perturbation equations to be solved:

zeroth:

$$[p^2/2 - E_0]\psi_0(\mathbf{p}) + \int U_0(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})d\mathbf{q} = 0, \tag{5a}$$

first:

$$[p^2/2 - E_0]\psi_1(\mathbf{p}) - E_1\psi_0(\mathbf{p}) + \int U_0(\mathbf{q})\psi_1(\mathbf{p}-\mathbf{q})d\mathbf{q} = 0, \tag{5b}$$

second:

$$[p^2/2 - E_0]\psi_2(\mathbf{p}) - E_1\psi_1(\mathbf{p}) - E_2\psi_0(\mathbf{p}) + \int [U_0(\mathbf{q})\psi_2(\mathbf{p}-\mathbf{q}) + U_1(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})]d\mathbf{q} = 0, \tag{5c}$$

and generally for $n \geq 2$,

nth:

$$[p^2/2 - E_0]\psi_n(\mathbf{p}) - \sum_{k=1}^{n} E_k\psi_{n-k}(\mathbf{p}) + \int [U_0(\mathbf{q})\psi_n(\mathbf{p}-\mathbf{q}) + \sum_{k=1}^{n-1} U_k(\mathbf{q})\psi_{n-k-1}(\mathbf{p}-\mathbf{q})]d\mathbf{q} = 0. \tag{5d}$$

The zeroth order equation (5a) is the Schrödinger equation for the hydrogen atom, and its solutions have been already known.[3,5-7] For the ground state, the result is

$$E_0 = -1/2, \tag{6a}$$

$$\psi_0(\mathbf{p}) = (2\sqrt{2}/\pi)(p^2+1)^{-2}, \quad p = |\mathbf{p}|. \tag{6b}$$

B. Fock transformation of momentum vector

We may project the three-dimensional momentum space onto the four-dimensional sphere with the origin at $\mathbf{p} = \mathbf{0}$ and the radius p_0.[3-5] The projective origin is taken at the point $(0, 0, 0, -p_0)$. Then a momentum vector $\mathbf{p} = (p, \theta, \phi)$ [or $=(p_x, p_y, p_z)$ in the Cartesian coordinates] in the hyperplane is transformed to a point on the hypersphere, which is specified by the three angles (α, θ, ϕ). The transformation is

$$p = p_0 \tan(\alpha/2), \quad \theta = \theta, \quad \phi = \phi; \tag{7a}$$

namely the two angles θ and ϕ have usual physical meaning, while the angle α $(0 \leq \alpha < \pi)$ represents p. The resultant relations are

$$\sin\alpha = 2pp_0/(p^2+p_0^2), \tag{7b}$$

$$\cos\alpha = (p_0^2 - p^2)/(p^2+p_0^2), \tag{7c}$$

$$d\mathbf{p} = [(p^2+p_0^2)/2p_0]^3 d\Omega, \tag{7d}$$

$$d\Omega = \sin^2\alpha \sin\theta \, d\alpha \, d\theta \, d\phi, \tag{7e}$$

where Ω means the collection of the new variables α, θ, and ϕ. In Eq. (7d) and hereafter, p is conveniently used to represent $p_0 \tan(\alpha/2)$ even after the Fock transformation is performed.

An important property, which motivates the introduction of the Fock transformation, is

$$|\mathbf{p} - \mathbf{p}'|^{-2} = 4p_0^2[4\sin^2(\omega/2)(p^2+p_0^2)(p'^2+p_0^2)]^{-1}, \tag{8}$$

where ω is the angle spanned between the two points (α, θ, ϕ) and $(\alpha', \theta', \phi')$, which are, respectively, the projections of the vectors $\mathbf{p}$ and $\mathbf{p}'$, on the surface of the hypersphere.[3-5] Furthermore, $[4\sin^2(\omega/2)]^{-1}$ can be expanded as[5]

$$[4\sin^2(\omega/2)]^{-1} = 2\pi^2 \sum_{nlm} n^{-1} Y^*_{nlm}(\Omega')Y_{nlm}(\Omega). \tag{9}$$

$Y_{nlm}(\Omega)$ is the four-dimensional spherical harmonic defined by[5]

$$Y_{nlm}(\Omega) = (-i)^l C_{n,l}(\alpha)Y_{lm}(\theta, \phi), \tag{10a}$$

where $Y_{lm}(\theta, \phi)$ is the usual (three-dimensional) spherical harmonic and

$$C_{n,l}(\alpha) = \{2n(n-l-1)!/[\pi(n+l)!]\}^{1/2} \sin^l\alpha \times [d^l C^1_{n-1}(\mu)/d\mu^l]_{\mu=\cos\alpha} \tag{10b}$$

in which $C^\nu_t(\mu)$ denotes the Gegenbauer polynomials. The Y_{nlm} are orthonormal in that

$$\int Y^*_{n'l'm'}(\Omega)Y_{nlm}(\Omega)d\Omega = \delta_{nn'}\delta_{ll'}\delta_{mm'} \tag{10c}$$

and satisfy

$$Y^*_{nlm}(\Omega) = (-1)^{l-m}Y_{nl-m}(\Omega). \tag{10d}$$

By the Fock transformation, the hydrogen $1s$ wave function $\psi_0(\mathbf{p})$ [Eq. (6b)] is expressed as

$$\psi_0(\Omega) = 4(p^2+1)^{-2}Y_{100}(\Omega) \tag{11a}$$

$$= (p^2+1)^{-1}[2Y_{100}(\Omega) + Y_{200}(\Omega)], \tag{11b}$$

where we have chosen $p_0 = \sqrt{-2E_0} = 1$ from the form of $\psi_0(\mathbf{p})$. Since a perturbation equation refers the results of all the lower orders and the lowest order solution $\psi_0(\Omega)$ is simply expressed by the four-dimensional spherical harmonics when the radius p_0 is unity, it seems to be most natural and convenient to discuss the perturbation wave functions using this value of p_0. Indeed, we see that only when $p_0 = 1$, solutions of the momentum-space perturbation equations are easily found in closed forms. For the sake of simplicity, we set $p_0 = 1$ in the following discussion, but we note that this value comes from the consideration of the structure of the equations to be solved.

III. SOLUTION

A. First order

From Eqs. (5b) and (6a), the first order energy E_1 is

$$E_1 = \frac{1}{2}\int \psi_0^*(\mathbf{p})(p^2+1)\psi_1(\mathbf{p})d\mathbf{p} + \int \psi_0^*(\mathbf{p})\left[\int U_0(\mathbf{q})\psi_1(\mathbf{p}-\mathbf{q})d\mathbf{q}\right]d\mathbf{p}$$

$$= \frac{1}{2}\int \psi_1(\mathbf{p})(p^2+1)\psi_0^*(\mathbf{p})d\mathbf{p} + \int \psi_1(\mathbf{p})\left[\int U_0(\mathbf{q})\psi_0^*(\mathbf{p}+\mathbf{q})d\mathbf{q}\right]d\mathbf{p}. \quad (12a)$$

However, the complex conjugate form of Eq. (5a) is

$$\tfrac{1}{2}(p^2+1)\psi_0^*(\mathbf{p}) + \int U_0(\mathbf{q})\psi_0^*(\mathbf{p}+\mathbf{q})d\mathbf{q} = 0, \quad (13)$$

since $U_0^*(\mathbf{q}) = U_0(-\mathbf{q})$. Then we see

$$E_1 = 0, \quad (12b)$$

and hence the first order perturbation equation takes the same form as the zeroth order one. It follows that $\psi_1(\mathbf{p})$ is a multiple of $\psi_0(\mathbf{p})$, and we may put

$$\psi_1(\mathbf{p}) = 0, \quad (14)$$

for the sake of simplicity.[2]

B. Second order

From Eq. (5c), the second order energy E_2 is

$$E_2 = \int \psi_0^*(\mathbf{p})\left[\int U_1(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})d\mathbf{q}\right]d\mathbf{p}, \quad (15a)$$

where we have used Eqs. (12b), (13), and (14). Using Eqs. (3d) and (6b), we find

$$\int U_1(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})d\mathbf{q} = i(8\sqrt{2}/\pi)p(p^2+1)^{-3}P_1(\cos\theta)$$
$$= -(p^2+1)^{-1}[2Y_{210}(\Omega) + (\sqrt{6}/3)Y_{310}(\Omega)], \quad (16)$$

from which E_2 is calculated to be [see also Eqs. (7d), (10c), and (11a)]

$$E_2 = -\int Y_{100}^*(\Omega)[Y_{210}(\Omega) + (\sqrt{6}/6)Y_{310}(\Omega)]d\Omega = 0. \quad (15b)$$

Since $E_1 = E_2 = \psi_1 = 0$, the second order perturbation equation (5c) now takes a form

$$(p^2+1)\psi_2(\mathbf{p}) + 2\int U_0(\mathbf{p}-\mathbf{p}')\psi_2(\mathbf{p}')d\mathbf{p}' - 2(p^2+1)^{-1} \times [2Y_{210}(\Omega) + (\sqrt{6}/3)Y_{310}(\Omega)] = 0, \quad (17a)$$

where we have changed the dummy variable $\mathbf{q}$ with $\mathbf{p}-\mathbf{p}'$ in the integral. When Eqs. (3c) and (8) are applied, Eq. (17a) becomes

$$(p^2+1)\psi_2(\Omega) - (2\pi^2)^{-1}(p^2+1)^{-1} \times \int [4\sin^2(\omega/2)]^{-1}(p'^2+1)^2\psi_2(\Omega')d\Omega' - 2(p^2+1)^{-1}[2Y_{210}(\Omega) + (\sqrt{6}/3)Y_{310}(\Omega)] = 0. \quad (17b)$$

Using the expansion (9) and substituting

$$\psi_2(\Omega) = (p^2+1)^{-2}\chi_2(\Omega), \quad (18a)$$

we see Eq. (17b) is simplified to

$$\chi_2(\Omega) - \sum_{nlm} n^{-1}Y_{nlm}(\Omega)\int Y_{nlm}^*(\Omega')\chi_2(\Omega')d\Omega' - 2[2Y_{210}(\Omega) + (\sqrt{6}/3)Y_{310}(\Omega)] = 0. \quad (17c)$$

From the orthonormality of $Y_{nlm}(\Omega)$ [Eq. (10c)], a solution is found to be

$$\chi_2(\Omega) = 8Y_{210}(\Omega) + \sqrt{6}Y_{310}(\Omega), \quad (19)$$

and therefore the second order wave function is

$$\psi_2(\Omega) = (p^2+1)^{-2}[8Y_{210}(\Omega) + \sqrt{6}Y_{310}(\Omega)]$$
$$= -i(4\sqrt{2}/\pi)p[(p^2+1)^{-3} + 6(p^2+1)^{-4}]P_1(\cos\theta), \quad (18b)$$

which is identical with the Dirac–Fourier transform[1] of the position-space solution.

C. Third order

Since $E_1 = E_2 = \psi_1 = 0$ and

$$\int U_2(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})d\mathbf{q} = (48\sqrt{2}/\pi)p^2(p^2+1)^{-4}P_2(\cos\theta)$$
$$= -(p^2+1)^{-1}[3\sqrt{2}Y_{320}(\Omega) + (3/2)Y_{420}(\Omega)] \quad (20)$$

from Eqs. (3e) and (6b), the third order energy E_3 is [from Eq. (5d) with $n = 3$]

$$E_3 = \int \psi_0^*(\mathbf{p})\left[\int U_2(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})d\mathbf{q}\right]d\mathbf{p}$$
$$= -\frac{1}{2}\int Y_{100}^*(\Omega)[3\sqrt{2}Y_{320}(\Omega) + (3/2)Y_{420}(\Omega)]d\Omega$$
$$= 0. \quad (21)$$

Therefore the third order perturbation equation to be solved is

$$(p^2+1)\psi_3(\mathbf{p}) + 2\int U_0(\mathbf{q})\psi_3(\mathbf{p}-\mathbf{q})d\mathbf{q} - 2(p^2+1)^{-1} \times [3\sqrt{2}Y_{320}(\Omega) + (3/2)Y_{420}(\Omega)] = 0. \quad (22a)$$

As the second order case, the Fock transformation simplifies this equation to

$$\chi_3(\Omega) - \sum_{nlm} n^{-1}Y_{nlm}(\Omega)\int Y_{nlm}^*(\Omega')\chi_3(\Omega')d\Omega' - [6\sqrt{2}Y_{320}(\Omega) + 3Y_{420}(\Omega)] = 0, \quad (22b)$$

where $\chi_3(\Omega)$ is defined by

$$\psi_3(\Omega) = (p^2+1)^{-2}\chi_3(\Omega). \quad (23a)$$

Equation (22b) has a solution

$$\chi_3(\Omega) = 9\sqrt{2}Y_{320}(\Omega) + 4Y_{420}(\Omega), \quad (23b)$$

and hence the third order wave function is

$$\psi_3(\Omega) = (p^2+1)^{-2}[9\sqrt{2}Y_{320}(\Omega) + 4Y_{420}(\Omega)]$$
$$= -(8\sqrt{2}/\pi)p^2[(p^2+1)^{-4} + 16(p^2+1)^{-5}]P_2(\cos\theta). \quad (23c)$$

D. Fourth order

Since $E_1 = E_2 = E_3 = \psi_1 = 0$, the explicit form of the fourth order perturbation equation is

$$\tfrac{1}{2}(p^2+1)\psi_4(\mathbf{p}) - E_4\psi_0(\mathbf{p}) + \int [U_0(\mathbf{q})\psi_4(\mathbf{p}-\mathbf{q}) + U_1(\mathbf{q})\psi_2(\mathbf{p}-\mathbf{q}) + U_3(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})]d\mathbf{p} = 0 \quad (24a)$$

from Eq. (5d). Using Eqs. (3d), (3f), (6b), and (18b), the two integrals appearing in the above equation are evaluated to be

$$\int U_1(\mathbf{q})\psi_2(\mathbf{p}-\mathbf{q})d\mathbf{q} = (4\sqrt{2}/\pi)\{[(p^2+1)^{-3} + 8(p^2+1)^{-4} - 16(p^2+1)^{-5}]P_0(\cos\theta) + [4(p^2+1)^{-3} + 28(p^2+1)^{-4} - 32(p^2+1)^{-5}]P_2(\cos\theta)\} = [2(p^2+1)]^{-1}[A'(\Omega) + B(\Omega)], \quad (25a)$$

$$\int U_3(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})d\mathbf{q} = (-i)(384\sqrt{2}/\pi)p^3(p^2+1)^{-5}P_3(\cos\theta) = [2(p^2+1)]^{-1}C(\Omega), \quad (25b)$$

where

$$A'(\Omega) = -9Y_{100}(\Omega) - 16Y_{200}(\Omega) - 14Y_{300}(\Omega) - 6Y_{400}(\Omega) - Y_{500}(\Omega), \quad (25c)$$

$$B(\Omega) = -11\sqrt{2}Y_{320}(\Omega) - 9Y_{420}(\Omega) - \sqrt{14/5}Y_{520}(\Omega), \quad (25d)$$

$$C(\Omega) = -12\sqrt{5}Y_{430}(\Omega) - 6\sqrt{2}Y_{530}(\Omega). \quad (25e)$$

Then the fourth order energy E_4 is

$$E_4 = \int \psi_0^*(\mathbf{p})\left\{\int [U_1(\mathbf{q})\psi_2(\mathbf{p}-\mathbf{q}) + U_3(\mathbf{q})\psi_0(\mathbf{p}-\mathbf{q})]d\mathbf{q}\right\}d\mathbf{p} = (1/4)\int Y_{100}^*(\Omega)[A'(\Omega) + B(\Omega) + C(\Omega)]d\Omega = -9/4. \quad (26)$$

Only the first term $[-9Y_{100}(\Omega)]$ of $A'(\Omega)$ contributes to E_4 owing to the orthonomality of $Y_{nlm}(\Omega)$. Using the Fock transformation followed by the substitution

$$\psi_4(\Omega) = (p^2+1)^{-2}\chi_4(\Omega), \quad (27)$$

we have the simplified fourth order equation

$$\chi_4(\Omega) - \sum_{nlm} n^{-1}Y_{nlm}(\Omega)\int Y_{nlm}^*(\Omega')\chi_4(\Omega')d\Omega' + A(\Omega) + B(\Omega) + C(\Omega) = 0, \quad (24b)$$

where

$$A(\Omega) = -2E_4(p^2+1)\psi_0(\Omega) + A'(\Omega) = -(23/2)Y_{200}(\Omega) - 14Y_{300}(\Omega) - 6Y_{400}(\Omega) - Y_{500}(\Omega). \quad (24c)$$

Since $A(\Omega)$, $B(\Omega)$, and $C(\Omega)$ have different l dependences, the solution $\chi_4(\Omega)$ of Eq. (24b) is decomposed into the three parts;

$$\chi_4(\Omega) = \chi_4^{l=0}(\Omega) + \chi_4^{l=2}(\Omega) + \chi_4^{l=3}(\Omega). \quad (28a)$$

The individual parts are found to be

$$\chi_4^{l=0}(\Omega) = -(89/4)Y_{100}(\Omega) + 23Y_{200}(\Omega) + 21Y_{300}(\Omega) + 8Y_{400}(\Omega) + (5/4)Y_{500}(\Omega) = -(2\sqrt{2}/\pi)[(31/4) + 6(p^2+1)^{-1} + 3(p^2+1)^{-2} + 32(p^2+1)^{-3} - 80(p^2+1)^{-4}]P_0(\cos\theta), \quad (28b)$$

$$\chi_4^{l=2}(\Omega) = (33\sqrt{2}/2)Y_{320}(\Omega) + 12Y_{420}(\Omega) + (\sqrt{70}/4)Y_{520}(\Omega) = -(2\sqrt{2}/\pi)p^2[5(p^2+1)^{-2} + 32(p^2+1)^{-3} + 160(p^2+1)^{-4}]P_2(\cos\theta), \quad (28c)$$

$$\chi_4^{l=3}(\Omega) = 16\sqrt{5}Y_{430}(\Omega) + (15\sqrt{2}/2)Y_{530}(\Omega) = i(32\sqrt{2}/\pi)p^3[(p^2+1)^{-3} + 30(p^2+1)^{-4}] \times P_3(\cos\theta). \quad (28d)$$

For the $\chi_4^{l=0}(\Omega)$ part, the coefficient $[-89/4]$ of $Y_{100}(\Omega)$ cannot be determined only from the perturbation equation (24b). We have determined it by the fourth order normalization condition given by

$$\int |\psi_2(\mathbf{p})|^2 d\mathbf{p} + \int [\psi_0^*(\mathbf{p})\psi_4(\mathbf{p}) + \psi_4^*(\mathbf{p})\psi_0(\mathbf{p})]d\mathbf{p} = 0, \quad (29)$$

which follows from the normalization of both the total and zeroth order wave functions, $\Psi(\mathbf{p})$ and $\psi_0(\mathbf{p})$, to unity. [Note that $\psi_1(\mathbf{p}) = 0$ in the present case.] The final result for the fourth order wave function $\psi_4(\Omega)$ is obtained by inserting Eqs. (28a)–(28d) into Eq. (27), which also agrees with the Dirac–Fourier transform of the position-space solution after the inverse Fock transformation.

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