Two electrons in an external oscillator potential: Particular analytic solutions of a Coulomb correlation problem

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The problem of the Schrödinger equation for two electrons (interacting with Coulomb potentials) in an external harmonic-oscillator potential is revisited and shown to be solvable analytically for a particular, denumerably infinite set of oscillator frequencies. Solutions are given for ground and excited states in the singlet and triplet spin configurations.

I. INTRODUCTION

There are few one-electron problems in quantum mechanics which can be solved analytically, for example the hydrogen atom or the harmonic oscillator, and even fewer many-body problems such as particles interacting with harmonic-oscillator potentials. We are going to draw attention to the fact that there is a system with genuine Coulomb correlations which is exactly solvable: two electrons in an external harmonic-oscillator potential. By "exactly solvable" we mean that the problem of a six-dimensional partial differential equation will be reduced to finding the real roots of a polynomial. However, the exact simple solution discussed here exists only for a certain infinite set of discrete oscillator frequencies. The solution comprises ground and excited states. Moreover, an approximate closed-form solution will be discussed which provides accurate results for small oscillator frequencies.

Former work on this problem comprises the analytical solution for the ground state of *one* particular oscillator frequency [1], solutions with an interparticle potential which necessarily has a linear term [2], perturbation theoretical treatments [3], and several numerical calculations [4–6]. We want to mention that the solution presented in [1] agrees with the simplest of our solutions.

There are many of applications for this system. The one considered here is to study the increasing importance of correlations with decreasing density in a finite system. This can be accomplished by turning down the oscillator frequency so that the wave function spreads out more and more. A similar study of the correlation effects has been done by Bryant [7] for a two-dimensional square well with infinitely high barriers solving the Schrödinger equation numerically. In a forthcoming paper [8] we studied the Wigner crystallization into a paired phase with two electrons per lattice site. In this case the external oscillator potential is provided by the compensating homogeneous background sphere. The ideas of the present paper can also be applied to the two-dimensional case, where a homogeneous magnetic field can be taken into account without additional complications [9]. This leads us directly to the analytical solution of the two-electron quantum dot. An application of quite another kind is the test of the approximations and numerical algorithms for the N-electron Coulomb correlation problem in an arbitrary external potential.

II. FACTORIZATION

To be self-contained, we first review the separation (see, e.g., [4]) of the Schrödinger equation into five equations which can be solved readily, and one radial Schrödinger equation of the interparticle coordinate which will be discussed in Sec. III. The Hamiltonian of the system in question reads*

$$H = -\tfrac{1}{2}\nabla_1^2 + \tfrac{1}{2}\omega^2 r_1^2 - \tfrac{1}{2}\nabla_2^2 + \tfrac{1}{2}\omega^2 r_2^2 + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \ , \qquad (1)$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position operators of the two particles. Atomic units $\hbar = m = e = 1$ are used throughout. Now we introduce the difference vector and the center of mass as new variables:

$$\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1 \ , \qquad (2)$$

$$\mathbf{R} = \tfrac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) \ , \qquad (3)$$

in which the Hamiltonian decouples:

$$H = -\nabla_r^2 + \tfrac{1}{4}\omega^2 r^2 + \frac{1}{r} - \tfrac{1}{4}\nabla_R^2 + \omega^2 R^2 \equiv H_r + H_R \ . \qquad (4)$$

Because H is independent of spin, the total wave function can be factorized as follows:

$$\psi(1,2) = \varphi(\mathbf{r})\xi(\mathbf{R})\chi(s_1, s_2) \ . \qquad (5)$$

The Pauli principle demands that if χ is symmetric against particle exchange (triplet state) then φ must be antisymmetric $[\varphi(-\mathbf{r}) = -\varphi(\mathbf{r})]$, and if χ is antisymmetric (singlet state) then we have $\varphi(-\mathbf{r}) = \varphi(\mathbf{r})$. In either case there is no constraint on $\xi(\mathbf{R})$ because $\mathbf{R}$ is symmetric in itself. Thus the Pauli principle is reduced to picking out solutions of definite parity and combining them with the appropriate spin part.

It follows from (4) that the Schrödinger equation $H\psi = E\psi$ separates into

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$$\left[-\tfrac{1}{2}\nabla_r^2+\tfrac{1}{2}\omega_r^2 r^2+\frac{1}{2}\frac{1}{r}\right]\varphi(\mathbf{r})=\varepsilon'\varphi(\mathbf{r}) \ , \tag{6}$$

where $\omega_r=\tfrac{1}{2}\omega$ and $\varepsilon'=\tfrac{1}{2}\varepsilon$, and

$$[-\tfrac{1}{2}\nabla_R^2+\tfrac{1}{2}\omega_R^2\mathbf{R}^2]\xi(\mathbf{R})=\eta'\xi(\mathbf{R}) \ , \tag{7}$$

where $\omega_R=2\omega$ and $\eta'=2\eta$. To establish a full analogy to well-known problems, we defined new oscillator frequencies and energies for either problem and the total energy is $E=\varepsilon+\eta$. The normalization condition for ψ can be split into $\int d\mathbf{r}|\varphi(\mathbf{r})|^2=1$ and $\int d\mathbf{R}|\xi(\mathbf{R})|^2=1$. The solution of the three-dimensional oscillator problem for the center of mass (7) is well known and needs no further consideration. Now we turn to the relative motion of both electrons. Here we introduce spherical coordinates which separate the modulus r from the angular coordinates $\hat{\mathbf{r}}=\mathbf{r}/r$, giving rise to the ansatz

$$\varphi(\mathbf{r})=\frac{u(r)}{r}Y_{lm}(\hat{\mathbf{r}}) \ , \tag{8}$$

where Y_{lm} are the spherical harmonics, and $u(r)$ is determined by the radial Schrödinger equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{1}{2}\omega_r^2 r^2+\frac{1}{2}\frac{1}{r}+\frac{l(l+1)}{2}\frac{1}{r^2}\right]u(r)=\varepsilon'u(r) \ . \tag{9}$$

Because of $Y_{lm}(-\hat{\mathbf{r}})=(-1)^l Y_{lm}(\hat{\mathbf{r}})$, we see that all eigensolutions satisfy the Pauli principle and that solutions corresponding to even (odd) l belong to the singlet (triplet) state.

III. SOLUTION OF THE RADIAL SCHRÖDINGER EQUATION

A. Approximate solution

Equation (9) defines an effective potential

$$V_{\text{eff}}=\tfrac{1}{2}\omega_r^2 r^2+\frac{1}{2}\frac{1}{r}+\frac{l(l+1)}{2}\frac{1}{r^2} \ , \tag{10}$$

which can be expanded around its minimum position r_0 in a Taylor series:

$$V_{\text{eff}}=V_0+\tfrac{1}{2}\omega_e^2(r-r_0)^2+\cdots \ , \tag{11}$$

where r_0 is the solution of

$$r_0^4-\frac{1}{2\omega_r^2}r_0-\frac{l(l+1)}{\omega_r^2}=0 \ , \tag{12}$$

and V_0 and ω_e are given by $V_0=V_{\text{eff}}(r_0)$ and $\omega_e^2=V_{\text{eff}}''(r_0)$. r_0 can be viewed as the classical distance of the electrons in the ground state. For $l=0$ we find a simple solution in closed form:

$$r_0=(2\omega_r^2)^{-1/3} \ , \tag{13}$$

$$V_0=\frac{3}{2}\left[\frac{\omega_r}{2}\right]^{2/3} \ , \tag{14}$$

$$\omega_e=\sqrt{3}\,\omega_r \ . \tag{15}$$

In any case, the approximate eigenvalues are

$$\varepsilon_m'=V_0+\omega_e[m+\tfrac{1}{2}] \ , \quad m=0,1,\ldots, \tag{16a}$$

and the approximate ground-state wave function is

$$u_0(r)=\left[\frac{\omega_e}{\pi}\right]^{1/4}e^{-(1/2)\omega_e(r-r_0)^2} \ ,$$

with V_0 and ω_e depending on l. It turns out that (16a) is the better, the smaller ω_r is (see Sec. IV). For large ω_r the electron density is high and the independent-particle picture (electron-electron interaction neglected) should apply, which gives

$$\varepsilon_m'=\omega_r[2m+\tfrac{3}{2}] \ , \quad m=0,1,\ldots . \tag{16b}$$

The curves for the ground state in both limiting cases are shown in Fig. 1. Obviously the independent-particle picture fails completely in describing the relative motion of the electrons for low densities or ω_r.

B. Exact solution

Introducing reduced variables into (9), $\rho=\sqrt{\omega_r}\,r, \varepsilon''=2\varepsilon'/\omega_r$, and splitting off the asymptotic solution for $r\to\infty$:

$$u(\rho)=e^{-(1/2)\rho^2}t(\rho) \ , \tag{17}$$

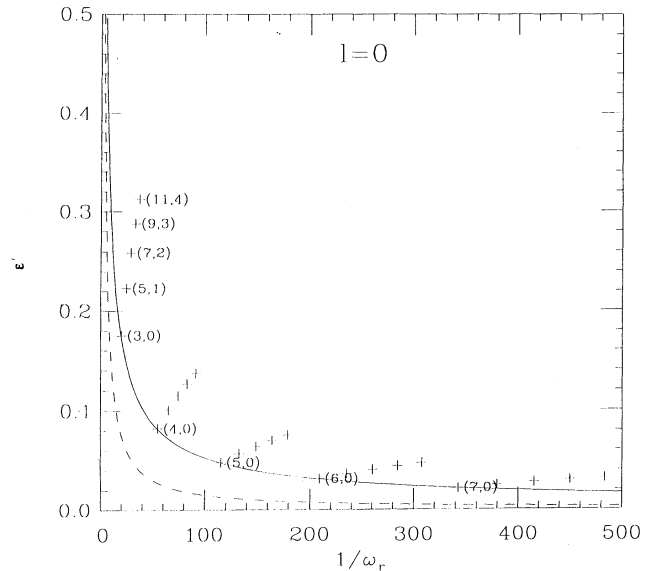FIG. 1. Exact solutions (crosses) for $l=0$ and $n<15$, which lie in the chosen ε' and ω_r ranges. Some solutions are supplemented by two numbers describing the order of the corresponding polynomial n and its number of zeros N_r. The full line is the result for the ground state in the Taylor-expansion approximation, and the dashed line refers to the independent-particle picture (electron-electron interaction is neglected).

leaves us with

$$\rho^2 t'' - 2\rho^3 t' + \left[(\varepsilon'' - 1)\rho^2 - \frac{1}{\sqrt{\omega_r}}\rho - l(l+1) \right] t = 0 \ . \quad (18)$$

A power-series expansion

$$t(\rho) = \rho^m \sum_{v=0}^{\infty} a_v \rho^v \ , \quad (19)$$

where $m = l + 1$ (the irregular solution $m = -l$ is dropped) transforms (18) into a recurrence relation for the coefficients a_v:

$$a_0 \neq 0 \ , \quad (20a)$$

$$a_1 = \frac{1}{2(l+1)\sqrt{\omega_r}} a_0 \ , \quad (20b)$$

$$a_v = \frac{1}{v(v+2l+1)} \left\{ \frac{1}{\sqrt{\omega_r}} a_{v-1} + [2(l+v) - 1 - \varepsilon'']a_{v-2} \right\} \quad \text{for } v \geq 2 \ . \quad (20c)$$

Now we are looking for the condition that defines the discrete eigenvalue spectrum. Unfortunately, this is not straightforward as for the harmonic-oscillator or the hydrogen problems, because (20) is a three-step recurrence relation. In our problem, termination of the power series, which guarantees normalization, can be reached in the following way. Using (20) we can determine a_v for arbitrary v:

$$a_v = F(l, v, \varepsilon'', \omega_r) a_0 \ . \quad (21)$$

Now we assume that the series of a_v terminates at a certain $v = n$:

$$\ldots, a_{n-1} \neq 0, \ a_n = 0 \ , \ a_{n+1} = 0, \ldots \ ,$$

so that the order of the polynomial $t(\rho)$ is $n + l$.

To reach this situation we must guarantee that $a_n = 0$ and $a_{n+1} = 0$. The first condition is fulfilled if

$$F(l, n, \varepsilon'', \omega_r) = 0 \ , \quad (22)$$

and for the second we rewrite (20c) as

$$a_{n+1} = \frac{1}{(n+1)(n+2l+2)} \times \left\{ \frac{1}{\sqrt{\omega_r}} a_n + [2(l+n+1) - 1 - \varepsilon'']a_{n-1} \right\} \ , \quad (23)$$

and find that the bracket in (23) must vanish:

$$\varepsilon'' = 2(l+n) + 1 \ . \quad (24)$$

Formulas (22) and (24) are two equations for ε'' and ω_r which must be fulfilled simultaneously and which define the energy spectrum. Unfortunately, we cannot find the energy spectrum for a *given* oscillator frequency ω_r straightforwardly. Equation (24) allows us to calculate the reduced energies ε'' for a given n and l. On the other hand, insertion of (24) into (22) provides an equation for ω_r:

$$F(l, n, 2(l+n) + 1, \omega_r) = 0 \ . \quad (25)$$

Thus (25) determines which oscillator frequency ω_r belongs to the reduced energy given by (24).

Finally, we want to mention that additional information about the function $\varepsilon'(\omega_r)$ can be obtained by application of the Hellman-Feynman theorem to Eq. (9), giving

$$\frac{d\varepsilon'}{d\omega_r} = \omega_r \int dr [u(r)]^2 r^2 \ .$$

This can be calculated exactly for those ω_r for which analytical solutions have been found.

C. Results

To make things more clear, we first consider some special cases. For $n = 2$ and arbitrary l, (24) provides the reduced energies

$$\varepsilon'' = 2l + 5 \quad (26)$$

and from (20a)–(20c), (21), and (24) follows

$$F(\omega_r) = \frac{1}{2(2l+3)} \left\{ \frac{1}{2(l+1)} \frac{1}{\omega_r} - 2 \right\} \ , \quad (27)$$

which has the zero

$$\omega_r = \frac{1}{4(l+1)} \ . \quad (28a)$$

Thus the energies for $n = 2$ and arbitrary l are

$$\varepsilon' = \frac{\omega_r}{2}\varepsilon'' = \frac{2l+5}{8(l+1)} \xrightarrow[l \to \infty]{} \frac{1}{4} \ . \quad (28b)$$

The corresponding radial wave functions $u(r)$ read (apart from a normalization factor)

$$u(r) = r^{(l+1)} e^{-r^2/8(l+1)} \left[1 + \frac{r}{2(l+1)} \right] \ . \quad (28c)$$

For $n = 3$ and arbitrary l, the solutions are

$$\omega_{\mathrm{r}} = \frac{1}{4(4l+5)} .$$ (29a)

$$\varepsilon' = \frac{2l+7}{8(4l+5)}$$ (29b)

$$u(r) = r^{(l+1)} e^{-r^2/8(4l+5)}$$

$$\times \left[1 + \frac{r}{2(l+1)} + \frac{r^2}{4(l+1)(4l+5)} \right] .$$ (29c)

Let us now consider the case $l=0$ and arbitrary n. In this case n is the order of the polynomial $t(\rho)$. The corresponding F's up to $n=11$ are easily calculated, giving rise to the solutions in Table I. (The result up to $n=5$ can be obtained in closed form.) We want to stress that solutions found in this way are not necessarily ground states. To which step of the excitation a solution belongs depends on the number of nodes of the polynomial $t(\rho)$ for $\rho > 0$. Generally, we find that for a given n, the number of real positive roots of the equation $F(\omega_{\mathrm{r}})=0$ is $N_\omega = \mathrm{int}(n/2)$, and that among the N_ω eigensolutions for $t(\rho)$ that with the smallest ω_{r} has zero nodes (ground state), that with the second largest ω_{r}, has one node (first-excited state), etc.

Some more solutions for $l=0$ are shown in Fig. 1. A practical way for finding the solution for a given ω_{r} and l is to calculate the solutions for some ω_{r} in the range of interest and to interpolate between the energy values. However, Fig. 1 and Table I demonstrate that for the most interesting case of small ω_{r} the Taylor expansion discussed in Sec. III A often might be good enough. An

TABLE I. Energies for $l=0$ and $n \leq 11$. N_r is the number of real positive nodes of $t(\rho)$ [and of $u(r)$], ε_T' is from the Taylor expansion for the ground state as described in Sec. III A, and $\varepsilon_{\mathrm{int}}'$ includes the improvement added in Sec. III C.

| n	$1/\omega_r$	N_r	ε'	ε_T'	$\dfrac{\varepsilon'-\varepsilon_T'}{\varepsilon'}$ (%)	$\varepsilon_{\mathrm{int}}'$	$\dfrac{\varepsilon'-\varepsilon_{\mathrm{int}}'}{\varepsilon'}$ (%)
2	4	0	0.6250	0.5915	5.36	0.6250	0 (fitted)
3	20	0	0.1750	0.1715	1.97	0.1750	−0.023
4	54.7386	0	0.0822	0.0814	1.02	0.0822	0.026
	5.26137	1	0.8553	0.8062	5.74	0.8553	0 (fitted)
5	115.299	0	0.0477	0.0474	0.63	0.0477	0.049
	24.7010	1	0.2227	0.2166	2.73	0.2228	−0.045
6	208.803	0	0.0311	0.0310	0.43	0.0311	0.055
	64.8131	1	0.1003	0.0986	1.63	0.1003	0.005
	6.38432	2	1.0181	0.9528	6.41	1.0181	0 (fitted)
7	342.366	0	0.0219	0.0218	0.31	0.0219	0.054
	132.638	1	0.0565	0.0559	1.11	0.0565	0.041
	28.9962	2	0.2587	0.2495	3.56	0.2588	−0.062
8	523.102	0	0.0162	0.0162	0.24	0.0162	0.050
	235.301	1	0.0361	0.0358	0.80	0.0361	0.058
	74.1774	2	0.1146	0.1119	2.35	0.1146	−0.019
	7.41903	3	1.1457	1.0655	7.00	1.1457	0 (fitted)
9	758.124	0	0.0125	0.0125	0.19	0.0125	0.045
	379.925	1	0.0250	0.0249	0.61	0.0250	0.064
	148.942	2	0.0638	0.0627	1.69	0.0638	0.022
	33.0088	3	0.2878	0.2755	4.28	0.2879	−0.045
10	1054.54	0	0.0100	0.0099	0.15	0.0100	0.041
	573.625	1	0.0183	0.0182	0.48	0.0183	0.064
	260.427	2	0.0403	0.0398	1.29	0.0403	0.047
	83.0152	3	0.1265	0.1227	3.01	0.1265	−0.004
	8.39091	4	1.2514	1.1577	7.48	1.2513	0 (fitted)
11	1419.47	0	0.0081	0.0081	0.12	0.0081	0.037
	823.515	1	0.0140	0.0139	0.39	0.0140	0.062
	415.764	2	0.0277	0.0274	1.02	0.0276	0.060
	164.445	3	0.0699	0.0683	2.27	0.0699	0.036
	36.8097	4	0.3124	0.2971	4.89	0.3123	0.035
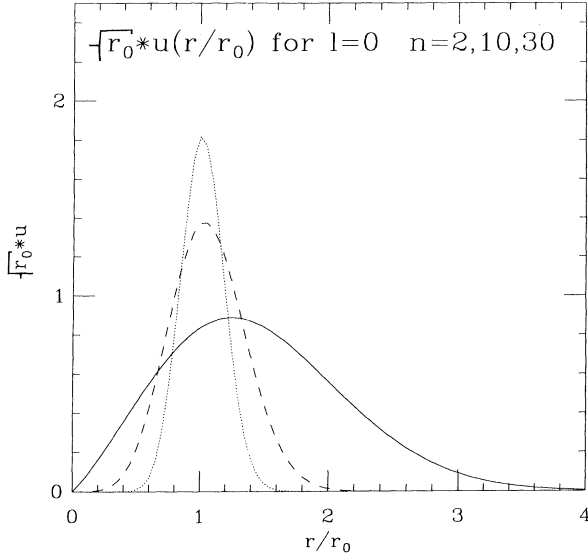
FIG. 2. Radial part $u(r)$ of the internal wave function $\varphi(\mathbf{r})$ for the ground states to $l=0$ and $n=2$ (full), 10 (dashed), and 30 (dotted), which belong to the solutions $\omega_r=0.25$, 9.4828×10^{-4}, and 3.2429×10^{-5}. r_0 is the classical electron distance as defined in Sec. III A.

FIG. 3. Electron density $n(\mathbf{r})$ corresponding to the solution shown in Fig. 2.

improved closed-form expression also for larger ω_r is obtained by interpolation between the small- ω_r approximation (16a) and the large- ω_r approximation (16b):

$$\varepsilon'_{int}=\frac{3}{2^{5/3}}\omega_r^{2/3}+\frac{C(2N_r+\frac{3}{2})\omega_r^P+\sqrt{3}(N_r+\frac{1}{2})\omega_r^{-P}}{C\omega_r^P+\omega_r^{-P}}\omega_r ,$$

(30)

where the constant C is fitted to reproduce the exact energy value for the lowest available $1/\omega_r$, and the exponent is optimized to provide the lowest rms error for the remaining exact energy values. In this way we find for $l=0$ and N_r from 0 to 4 for C the values 0.521 245, 0.833 802, 1.162 25, 1.511 11, and 1.915 76, and for P the values 0.24, 0.22, 0.20, 0.19, and 0.19. The results of this interpolation formula are also shown in Table I. As seen, the accuracy of this interpolation formula is better than 0.1%. Of course, any approximation in finding the solution for a given ω_r can be avoided by resorting to a numerical solution of the ordinary differential equation (9) by standard methods.

IV. DISCUSSION

In this section we will discuss some physical consequences. Correlations are most appropriately discussed by means of the pair-correlation function:

$$G(\mathbf{r})=\left\langle\psi\left|\sum_{i<j}\delta(\mathbf{r}_i-\mathbf{r}_j-\mathbf{r})\right|\psi\right\rangle$$

$$=\int d^3r'|\psi(\mathbf{r}+\mathbf{r}',\mathbf{r}')|^2$$

$$=|\varphi(\mathbf{r})|^2 ,$$

which is determined by the internal wave function $\varphi(\mathbf{r})$ only. In Fig. 2 the radial part $u(r)$ of $\varphi(\mathbf{r})$ is given for $l=0$ and three ω_r values. We see that the probability for the electrons to have a certain distance r gathers around the classical distance r_0. The variance of the distribution is smaller than the smaller ω_r, and consequently the density, is. This is obvious because for decreasing density the interaction energy dominates and governs the properties (as in the Wigner crystal). The same tendency is seen in the charge density:

$$n(\mathbf{r})=\left\langle\psi\left|\sum_i\delta(\mathbf{r}-\mathbf{r}_i)\right|\psi\right\rangle$$

$$=2\int d^3r'|\varphi(\mathbf{r}')|^2\left|\xi\left[\mathbf{r}+\frac{\mathbf{r}'}{2}\right]\right|^2 ,$$

which is a convolution integral between the internal and center-of-mass motions, and which is drawn in Fig. 3. For high densities, correlations are unimportant and both electrons seek independently from each other to minimize the potential energy in the external potentials. This results in a density centered at the origin. In this limit a one-particle picture applies. But with decreasing ω_r the importance of correlations increases and the electrons approach a model where they are distributed on a sphere shell with diameter r_0. Thereby they are always located at antipodal points. The last fact follows immediately from the pair-correlation function.

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