Four electrons interacting pairwise in the limit of infinitesimal confining potentials: especially the quintet spin state.

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In very recent work, Amovilli and March have considered the Hookean atom with four electrons. In particular, they demonstrated the cross-over from a triplet P_g ground state at large harmonic force constant k to a quintet S_u configuration for weak confinement, by means primarily of diffusion quantum Monte Carlo simulation. Here, we focus on such a quintet state for again 4 spin half fermions but now interacting via a harmonic pair force $-Kr_{ij}$. The spatial quintet Ψ is then available, with its eigenvalue. Progress on calculating low-order spinless density matrices is recorded. Finally, this prompts us to examine the Amovilli-March results when extrapolated to small $k \neq 0$. We display as $k \rightarrow 0^+$ approximate results for the four-electron Hookean atom model, including fitted analytic forms for kinetic and Coulomb energy as a function of k as $k \rightarrow 0^+$.

Keywords: Density matrix, Moshinsky atom, Hookean atom

A very recent study by Amovilli and March [1] of the Hookean atom with four Coulombically repelling electrons has had recourse to diffusion quantum Monte Carlo (DQMC) simulations. The authors demonstrated thereby, for a harmonic confining external potential $V_{ext}(r)$ given by

$$V_{ext}(r) = \frac{1}{2}kr^2 \quad (1)$$

that, as k is varied from strong to weak values, there is a cross-over from a triplet ground-state 3P_g to a quintet configuration 5S_u , the 3P_g being lowest in energy for large k .

Here, we first complement the above DQMC study for the four-electron Hookean atom by re-opening the Moshinsky model [2], but now for four electrons. However, to make analytical progress, we first put $k = 0^+$ in Eq.(1) and consider the four electrons moving under the influence of a central pairwise interaction $V(r_{ij})$ given, following [2] for two electrons by

$$V(r_{ij}) = \frac{1}{2}Kr_{ij}^2. \quad (2)$$

Prompted by the comments on [1] made above, we shall restrict ourselves to the quintet, $S = 2$, state, however. It is then fortunate that the wave function, denoted below by $\Psi^{(2S+1)} = \Psi^{(5)}$, is known, its calculation going back, at very least, to Bruch [3].

The form of $\Psi^{(5)}$ is then given by (see Eqs.(12), (1) and (36) of [3]) as a product of a spatial wave function B and a spin function. Since we shall work with the reduced spatial density matrices Γ_n of Löwdin [4] below, we need not concern ourselves with the spin function. But B is known and hence we can write the spatial four-electron $\Psi^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$ explicitly as (Eq.(36) of [3]), in unnormalized form:

$$\Psi^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \mathbf{u} \cdot (\mathbf{v} \times \mathbf{w}) \exp Q. \quad (3)$$

Bruch gives the RHS of Eq.(3), explicitly defining $\mathbf{u}$ to Q as follows:

$$\mathbf{u} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2) - \frac{1}{2}(\mathbf{r}_3 + \mathbf{r}_4), \quad (4)$$

$$\mathbf{v} = \mathbf{r}_1 - \mathbf{r}_2, \mathbf{w} = \mathbf{r}_3 - \mathbf{r}_4 \quad (5)$$

and

$$Q = -\frac{m\omega_I}{4\hbar}(2u^2 + v^2 + w^2). \quad (6)$$

Here ω_I is related to K introduced in Eq.(2) by

$$\omega_I^2 = \frac{K}{m} \quad (7)$$

Defining, as in [3], an energy unit ϵ by

$$\epsilon = \hbar \left(\frac{K}{m} \right)^{(1/2)} \quad (8)$$

the quintet wave function Eq.(3) corresponds to total energy 15ϵ [3].

It is evident that with total Hamiltonian $\hat{H}$, which separates into a centre-of-mass kinetic energy term and three decoupled oscillators, we can then write the 'local energy' equation as

$$15\epsilon = \frac{\hat{H}\Psi^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)}{\Psi^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)} \quad (9)$$

Following, for example, Dawson and March [5], we can reduce the above Eq.(9) by straightforward manipulation into an equation of such local energy form relating solely the reduced density matrices $\Gamma^{(3)}, \Gamma^{(2)}$ and $\gamma(\mathbf{r}'_1, \mathbf{r}_1)$. The integration of $\Gamma^{(3)}$ to find the exact correlated $\Gamma^{(2)}$ involves fairly extensive but straightforward manipulation. It leads to the closed form of $\Gamma^{(2)}$ as

$$\begin{aligned} \Gamma^{(2)}(\mathbf{r}'_1, \mathbf{r}'_2; \mathbf{r}_1, \mathbf{r}_2) = & \frac{\sqrt{2}\pi^3\hbar^4}{2m^4\omega^4} \left\{ \left(\frac{4\hbar}{m\omega} - |\mathbf{R} - \mathbf{R}'|^2 \right) \mathbf{r} \cdot \mathbf{r}' + (\mathbf{R} \cdot \mathbf{r})(\mathbf{R} \cdot \mathbf{r}') + (\mathbf{R}' \cdot \mathbf{r})(\mathbf{R}' \cdot \mathbf{r}') \right. \\ & \left. - (\mathbf{R}' \cdot \mathbf{r})(\mathbf{R} \cdot \mathbf{r}') - (\mathbf{R} \cdot \mathbf{r})(\mathbf{R}' \cdot \mathbf{r}') \right\} e^{-\frac{m\omega}{4\hbar}(|\mathbf{R} - \mathbf{R}'|^2 + \mathbf{r}^2 + \mathbf{r}'^2)} \end{aligned} \quad (10)$$

where $\mathbf{r}$ and $\mathbf{R}$ are defined (the primed quantities are defined in the same way but with primes instead) by

$$\mathbf{R} = \frac{\mathbf{r}_1 + \mathbf{r}_2}{2}, \quad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \quad (11)$$

The diagonal element of Eq.(10) is the very important pair density $P(r) = \Gamma^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2)$ where $r = |\mathbf{r}_1 - \mathbf{r}_2|$. $P(r)$ is then of the form

$$P(r) = \frac{2\sqrt{2}\pi^3\hbar^5}{m^5\omega^5} r^2 e^{-\frac{m\omega}{2\hbar}r^2}. \quad (12)$$

But equally important is the 1DM $\gamma(\mathbf{r}'_1, \mathbf{r}_1)$, which is given by

$$\gamma(\mathbf{r}'_1, \mathbf{r}_1) = \int \Gamma^{(2)}(\mathbf{r}'_1, \mathbf{r}_2; \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (13)$$

with $\Gamma^{(2)}$ in Eq.(10) after putting $\mathbf{r}'_2 = \mathbf{r}_2$. The result has the form

$$\gamma(\mathbf{r}'_1, \mathbf{r}_1) = 24\pi^{\frac{9}{2}} \left(\frac{\hbar}{m\omega} \right)^{\frac{11}{2}} \left\{ \frac{\hbar^2}{m^2\omega^2} - \frac{\hbar}{8m\omega} r^2 \right\} e^{-\frac{3m\omega}{16\hbar}r^2} \quad (14)$$

where here r denotes $|\mathbf{r}_1 - \mathbf{r}'_1|$. To proceed to relate the pair density $P(r)$ to $\gamma(\mathbf{r}'_1, \mathbf{r}_1) = \gamma(|\mathbf{r}_1 - \mathbf{r}'_1|)$, we note next that from Eq.(12)

$$\frac{m^5\omega^5 P(r)}{2\sqrt{2}\pi^3\hbar^5 r^2} = e^{-\frac{m\omega}{2\hbar}r^2}. \quad (15)$$

Taking logarithms of Eq.(15) yields immediately that

$$-\frac{m\omega}{2\hbar}r^2 = \ln \frac{m^5\omega^5 P(r)}{2\sqrt{2}\pi^3\hbar^5 r^2}. \quad (16)$$

This can be substituted into Eq.(14) with the result that

$$\gamma(\mathbf{r}'_1, \mathbf{r}_1) = 24\pi^{\frac{9}{2}} \left(\frac{\hbar}{m\omega} \right)^{\frac{11}{2}} \left\{ \frac{\hbar^2}{m^2\omega^2} + \frac{1}{16} \ln \frac{m^5\omega^5 P(r)}{2\sqrt{2}\pi^3\hbar^5 r^2} \right\} \left(\frac{m^5\omega^5 P(r)}{2\sqrt{2}\pi^3\hbar^5 r^2} \right)^{\frac{3}{8}} \quad (17)$$

It remains to eliminate ω from Eq.(17) to find what from the theorems of DFT could be a universal relationship in systems with translational invariance. Returning to Eq.(14) and taking its diagonal form yields

$$n(r) = \gamma(\mathbf{r}_1, \mathbf{r}_1) = \gamma(0) = 24\pi^{\frac{9}{2}} \left(\frac{\hbar}{m\omega} \right)^{\frac{15}{2}}. \quad (18)$$

Hence we find

$$\frac{\hbar}{m\omega} = \left(\frac{\gamma(0)}{24\pi^{\frac{9}{2}}} \right)^{\frac{2}{15}} \quad (19)$$

and therefore we relate through Eq.(17) and Eq.(19) the γ and $\Gamma^{(2)}$ via the diagonal (constant) element of $\gamma(r)$ given in Eq.(19).

To conclude this letter, we return to the Hookean atom with four electrons in [1] in the limit of weak harmonic confinement $k \rightarrow 0$. Then in Fig.1 we have plotted the result for T versus $\omega = (\frac{k}{m})^{1/2}$, where T is the total kinetic energy. We have used both the definitions of kinetic energy tabulated in Table II by Amovilli and March [1]. The dashed curve shown is motivated by the study of Cioslowski and Grzebielucha [6]. These authors found the exact limiting behavior of the total energy E for four electrons trapped in harmonic external potential as $k \rightarrow 0^+$. The leading terms from their result read

$$E = \frac{9}{2^{2/3}} \omega^{2/3} + \frac{1}{4} (6 + 4\sqrt{3} + 3\sqrt{6}) \omega + \dots \quad (20)$$

The curve of Fig.1 is then the plotted term

$$T = -0.22 \omega^{2/3} + 3.54 \omega. \quad (21)$$

Turning to Fig.2, this depicts the Coulomb potential U_c , data being again taken from Table II of [1], and used in the relation $U_c = (2/3)(U - T)$ obtained from the virial theorem, U being the total potential energy including the external potential contribution. With the same functional form, the analytical fit is

$$U_C = 4.00 \omega^{2/3} - 1.02 \omega. \quad (22)$$

In summary, the achievements of this letter are (a) concerned with the four-electron Moshinsky model and (b) the weak trapping limit of the analogous Hookean atom to (a). For this model (a), we can get some exact analytical relations for low-order spinless density matrices. Finally, we stress the key results in Eq.(17) and Eq.(19), which in the translationally invariant four-electron model relate the one and two DMs; a long-term aim of many-body theory.

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FIG. 1: Total kinetic energy T of Hookean atom with four Coulombically repelling electrons as function of confining force constant k in Eq.(1), where ω^2 is proportional to k . Note that both forms of kinetic energy obtained from the quantum Monte Carlo calculation in [1] have been used. The dashed curve shows the fitted analytic curve displayed in Eq.(21).

FIG. 2: Shows plot of Coulomb potential energy U_c versus ω for Hookean atom with four electrons. Crosses show results of Amovilli and March [1] using diffusion QMC calculations. Dashed curve is given by Eq.(22) of text, motivated by the analytic work for small ω in [6].