J Math Chem (2013) 51:1515–1520
DOI 10.1007/s10910-013-0151-x

ORIGINAL PAPER

Weak harmonic confinement of the quintet solution of a Moshinsky atom with 4 electrons

M. L. Glasser · N. H. March · L. M. Nieto

Received: 5 December 2012 / Accepted: 15 February 2013 / Published online: 26 March 2013

Abstract Bruch, in early work, treated a spatially free Moshinsky atom with four parallel-spin electrons interacting harmonically. Here we add a harmonic external potential, having an unrelated spring constant k, and use the variational method, with a one-parameter trial wave function, to examine the quintet ground state energy and electron density, particularly in the weak confinement limit $k \to 0$. The results are compared with Bruch's and modest contact is made with the early work of Post.

Keywords Moshinsky atom · Harmonic confinement · Beryllium · Quintet state

1 Introduction

Model two-electron atoms with harmonic confinement, going back at least to the work of Moshinsky [1], have now been solved for arbitrary electron-electron interaction $u(r_{12})$ by Holas et al. [2]. A recent study by Amovilli and March [3] of the Hookean atom with four Coulombically repelling electrons employed diffusion quantum Monte-Carlo (DQMC) simulations. These authors demonstrated that, for an external confining potential $V_{ext}(\vec{r})$ given by

M. L. Glasser (✉)
Department of Physics, Clarkson University, Potsdam, NY 13676, USA
e-mail: laryg@clarkson.edu

N. H. March
Department of Physics, University of Antwerp, Antwerp, Belgium

N. H. March
Oxford University, Oxford, England

L. M. Nieto
Departamento de Física Teórica, Atómica y Óptica, Facultad de Ciencias,
University of Valladolid, 40007 Valladolid, Spain

$$V_{ext}(r) = \frac{1}{2}kr^2, \tag{1.1}$$

as k was 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 ${}^3P_g$ state being lowest in energy for large k.

In the present article, we shall restrict attention to the Moshinsky-Post atom with four-electrons in the quintet $S = 2$ state. It is then fortunate that the exact wave function, denoted below by Ψ_B, is known in the limit of infinitesimal confinement ($k \to 0$ in (1.1)) from calculations going back, at least, to Bruch [4] in 1980. To summarize, the four electron spatial wave function $\Psi_B(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4)$ in unnormalized form can be written

$$\Psi_B(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4) = \vec{u} \cdot (\vec{v} \times \vec{w}) e^Q, \tag{1.2}$$

where

$$\vec{u} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2) - \frac{1}{2}(\vec{r}_3 + \vec{r}_4), \tag{1.3}$$

$$\vec{v} = \vec{r}_1 - \vec{r}_2, \quad \vec{w} = \vec{r}_3 - \vec{r}_4, \tag{1.4}$$

and

$$Q = -\frac{m\Omega}{4\hbar}(2u^2 + v^2 + w^2). \tag{1.5}$$

To this notation we also add the center of mass coordinate

$$\vec{R} = \frac{1}{4}(\vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \vec{r}_4). \tag{1.6}$$

In (1.5) Ω is related to the strength K of the harmonic electron-electron interaction

$$U(r_{ij}) = \frac{1}{2}Kr_{ij}^2 \tag{1.7}$$

by

$$\Omega^2 = \frac{K}{m}. \tag{1.8}$$

Defining, as in [1] an energy unit

$$\varepsilon = \hbar\Omega \tag{1.9}$$

the quintet wave-function above corresponding to total energy 15ε.

With this background, we turn immediately to make a variational generalization of Bruch's wave-function, designed for weak force constant k in the external potential (1.1).

2 Generalization of Bruch's wave function for small non-zero k

Denoting the Hamiltonian yielding the Bruch $k \to 0$ limit of Ψ given in (1.2) by $\hat{H}_B$ we now proceed variationally for the lowest quintet state of the Hamiltonian $\hat{H}$ defined by

$$\hat{H} = \hat{H}_B + \sum_{j=1}^{4} V_{ext}(r_j), \tag{2.1}$$

where V_{ext} is given (1.2). The variational generalization of Ψ_B proposed immediately below we have designed appropriately to describe $k \neq 0$ in (1.1), but remaining small.

We begin with Bruch's observation that the 4-electron Moshinsky Hamiltonian can be decomposed into free center-of-mass motion and harmonic oscillation with respect to the variables in (1.3), (1.4):

$$\hat{H}_B = \frac{1}{8m} P_R^2 + \hat{H}_u + \hat{H}_v + \hat{H}_w, \tag{2.2}$$

where

$$\begin{aligned} \hat{H}_u &= \frac{1}{2m} p_u^2 + 2Ku^2 \\ \hat{H}_v &= \frac{1}{m} p_v^2 + Kv^2 \\ \hat{H}_w &= \frac{1}{m} p_w^2 + Kw^2. \end{aligned} \tag{2.3}$$

We also note that, with (1.1) as the external potential, (2.1) becomes

$$\begin{aligned} \hat{H} &= \hat{H}_B + \hat{H}_c \\ \hat{H}_c &= 2kR^2 - \frac{\hbar k}{m\Omega} Q, \end{aligned} \tag{2.4}$$

with Q defined in (1.5). Also, because the transformation $\{\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4\} \to \{\vec{R}, \vec{u}, \vec{v}, \vec{w}\}$ is linear with unit Jacobian we can work in terms of the latter set of variables with no complications. We now choose the one-parameter trial wave function

$$\Phi(\vec{R}, \vec{u}, \vec{v}, \vec{w}) = \Psi_B e^{-\alpha R^2} \tag{2.5}$$

with Ψ_B given in (1.2), for which $\hat{H}_B \Psi_b = 15\varepsilon$. Thus, it is easily seen that

$$\mathcal{E}(\alpha) = \frac{< \Phi|\hat{H}|\Phi >}{< \Phi|\Phi >} = 15\varepsilon + \frac{3\alpha\hbar^2}{4m} + \left(2k - \frac{\alpha^2\hbar^2}{2m}\right) < R^2 > - \frac{\hbar k}{m\Omega} < Q > . \tag{2.6}$$

Also $< R^2 >= 3/4\alpha$ and $< Q >= -(\Omega/2)\partial \ln < \Psi_B|\Psi_B > /\partial\Omega$. We therefore require the normalization constant for (1.2), which is not given in [1] and for which the evaluation is complicated somewhat by the triple product in (1.2). However, with respect to spherical coordinates with $\vec{u}$ along the polar axis,

$$[\vec{u} \cdot (\vec{v} \times \vec{w})]^2 = u^2 v^2 w^2 \sin^2\theta_v \sin^2\theta_w \sin^2(\phi_v - \phi_w). \tag{2.7}$$

Hence,

$$\begin{aligned} < \Psi_B|\Psi_B > = 4\pi \int_0^\infty du u^4 e^{-\frac{m\Omega}{2\hbar}u^2} \left[\int_0^\infty dv v^4 e^{-\frac{m\Omega}{4\hbar}v^2}\right]^2 \\ \times \left[\int_0^\pi d\theta \sin^3\theta\right]^2 \int_0^{2\pi} d\phi_v \int_0^{2\pi} d\phi_w \sin^2(\phi_v - \phi_w). \end{aligned} \tag{2.8}$$

All the integrations in (2.8) are elementary, yielding $< \Psi_B|\Psi_B > = 192\,\pi^{9/2}(\hbar/m\Omega)^{15/2}$ whose logarithmic derivative with respect to Ω is $-15/2\Omega$. Thus,

$$\mathcal{E}(\alpha) = 15\varepsilon + \frac{3\alpha\hbar^2}{8m} + \frac{3k}{2\alpha} - 15\frac{\hbar k}{4m\Omega}. \tag{2.9}$$

The minimum energy

$$\mathcal{E}_0 = \varepsilon\left[15 + \frac{3}{4}\sqrt{\frac{k}{K}} - \frac{15}{4}\left(\frac{k}{K}\right)\right] \tag{2.10}$$

occurs for $\alpha = \sqrt{4mk}/\hbar$.

3 Electron density

The next task is to evaluate the one-electron density normalized to four electrons, which we write as the twelvefold integral

$$\rho(\vec{r}) = C\int d\vec{u}\, d\vec{v}\, d\vec{w}\, d\vec{R}\, \delta\left[\vec{r} - \vec{R} + \frac{1}{2}(\vec{u} + \vec{w})\right] e^{-2\alpha R^2} e^{2Q} [\vec{u} \cdot (\vec{v} \times \vec{w})]^2, \tag{3.1}$$

where C is a normalization constant. After the immediate $\vec{R}-$ integration it is simplest to use rectangular coordinates and set $\vec{r} = (0, 0, r)$. Thus we are left with the ninefold integral

$$\rho(r) = -Ce^{-2\alpha r^2} \int_{-\infty}^{\infty} du_1 \dots dw_3 e^{-\alpha L - S} \begin{vmatrix} u_1 & u_2 & u_3 \\ v_1 & v_2 & v_3 \\ w_1 & w_2 & w_3 \end{vmatrix}^2, \tag{3.2}$$

where

$$L = 2r(u_3 + w_3) + u_1 w_1 + u_2 w_2 + u_3 w_3 \tag{3.3a}$$

$$S = \frac{1}{2}\left(\alpha + \frac{2m\Omega}{\hbar}\right)\left(u_1^2 + u_2^2 + u_3^2\right) + \frac{1}{2}\left(\alpha + \frac{m\Omega}{\hbar}\right)\left(w_1^2 + w_2^2 + w_3^2\right) + \frac{m\Omega}{2\hbar}\left(v_1^2 + v_2^2 + v_3^2\right). \tag{3.3b}$$

Evaluating (3.2) is tedious, but is eased by the fact that all the integrals are Gaussian and there is no need to keep track of constant pre-factors, as they can be absorbed into C. The final result , after normalizing the density to $4e$ is

$$\rho(r) = \frac{16e}{3\pi(6\pi)^{1/2}} \frac{3\alpha + 2m\Omega/\hbar}{3\alpha + 2m\Omega/\hbar + 9\alpha^2} e^{-\lambda r^2}(1 + \beta r^2), \tag{3.4}$$

where

$$\lambda = \frac{4\alpha m\Omega}{(3\hbar\alpha + 2m\Omega)}$$

$$\beta = \frac{4\alpha^2}{3\alpha + 2m\Omega/\hbar}.$$

Finally, from (3.4) we can calculate the potential energy term

$$\int \rho(r) V_{ext}(r) d\vec{r} = \frac{3e\hbar k\left(5\beta + \frac{8\alpha m\Omega}{\hbar}\right)}{4\alpha m\Omega\left(3\beta + \frac{8\alpha m\Omega}{\hbar}\right)}. \tag{3.5}$$

4 Summary and future directions

In this work we have generalized the exact limiting result of Bruch [1], valid as $k \to 0$ in (1.1), for four electrons in the lowest quintet state, having exact wave function Ψ_B in (1.2) and corresponding energy 15ε. Our proposed variational wave-function can only be expected to be qualitatively useful when k remains small. But, most importantly, we have generated from the proposed variational function, the corresponding inhomogeneous electron density, while, of course, the infinitesimal confinement limit, solved by Bruch, corresponds to an (infinitesimal) constant density.

Finally, we have used the variational density to calculate the potential energy term $\int \rho(r) V_{ext}(r) d\vec{r}$.

Acknowledgments The work of MLG has been partially supported by the Spanish Ministerio de Educación y Ciencia (Project MTM 2005-09183) and he wishes to thank the University of Valladolid for continuing hospitality. NHM wishes to acknowledge that his contribution to this study was brought to fruition during a visit to the University of Valladolid and thanks Profs. J. A. Alonso and M.J. López for their generous hospitality. He also acknowledges support from Profs D. Lamoen and C. Van Alsenoy that makes possible continued affiliation with the University of Antwerp.

References

1. M. Moshinsky, Am. J. Phys. **36**, 52, (1968); (see also H.R. Post, Proc. Phys. Soc. **A66**, 649 (1953))
2. A. Holas, I.A. Howard, N.H. March, Phys. Lett. **A310**, 451 (2003)
3. C. Amovilli, N.H. March, Phys. Rev. **A83**, 044502 (2011)
4. L.W. Bruch, J. Chem. Phys. **72**, 5511 (1980)