J Math Chem (2014) 52:174–177
DOI 10.1007/s10910-013-0252-6

ORIGINAL PAPER

Perturbation theory for confined systems

Francisco M. Fernández

Received: 11 June 2013 / Accepted: 16 August 2013 / Published online: 24 August 2013

Abstract We discuss the application of perturbation theory to a system of particles confined in a spherical box. A simple argument shows that the particles behave almost independently in sufficiently strong confinement. We choose the helium atom with a moving nucleus as a particular example and compare results of first order with those for the nucleus clamped at the center of the box. We provide a suitable explanation for some numerical results obtained recently by other authors.

Keywords Confined systems · Perturbation theory · Helium atom

1 Introduction

In a recent paper Montgomery et al. [1] solved the Schrödinger equation for a He atom with its nucleus clamped at the origin of a box of radius R_c with impenetrable walls. They applied perturbation theory for the case of strong confinement (sufficiently small R_c) and obtained the first five coefficients of the expansion (with different degrees of accuracy). One of the conclusions in that paper was that the interaction between the electrons decreases with the box radius. The authors illustrated this behavior by means of the overlap between the wavefunctions for the confined He^+ and for the free electron in the box.

The purpose of this paper is to discuss those numerical results from a more general point of view. To this end in Sect. 2 we apply perturbation theory to a system of N particles in a spherical box and discuss the behaviour of a more general overlap integral. As a particular example, we compare the energies (corrected through first order) of

F. M. Fernández (✉)
División Química Teórica, INIFTA (UNLP, CCT La Plata-CONICET),
Diag. 113 y 64 (S/N), Sucursal 4, Casilla de Correo 16, 1900 La Plata, Argentina
e-mail: fernande@quimica.unlp.edu.ar

the He atom when the nucleus is clamped at the center of the box and when it moves within the box. Finally, in Sect. 3 we comment on the results and draw conclusions.

2 Perturbation theory for strong confinement

We consider a system of N particles of masses m_i and charges q_i. The nonrelativistic Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{i=1}^{N}\frac{\nabla_i^2}{m_i} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \tag{1}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the pair of particles located at $\mathbf{r}_i$ and $\mathbf{r}_j$.

If the system is confined in a box of radius R_c with impenetrable walls, any solution ψ to the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi \tag{2}$$

should vanish when $r_i = |\mathbf{r}_i| \geq R_c$ for any given particle i. In order to apply perturbation theory in the case of strong confinement $R_c \to 0$ we first convert the Schrödinger equation (2) into a more convenient dimensionless eigenvalue equation. We choose a representative particle (say $i = 1$) and define dimensionless masses $m_i' = m_i/m_1$, charges $q_i' = q_i/q_1$ and coordinates $\mathbf{r}_i' = \mathbf{r}_i/R_c$ ($\nabla_i' = R_c\nabla_i$). We thus obtain a dimensionless Hamiltonian operator

$$\hat{H}_d = \frac{m_1 R_c^2}{\hbar^2}\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\frac{\nabla_i'^2}{m_i'} + \lambda\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\frac{q_i' q_j'}{r_{ij}'}$$
$$\lambda = \frac{R_c}{a},\ a = \frac{4\pi\epsilon_0\hbar^2}{m_1 q_1^2} \tag{3}$$

and the dimensionless eigenvalue equation

$$\hat{H}_d\varphi = \epsilon\varphi,\ \epsilon = \frac{m_1 R_c^2}{\hbar^2}E = \frac{m_1 a^2\lambda^2}{\hbar^2}E \tag{4}$$

The new boundary conditions are $\varphi = 0$ if any $r_i' = |\mathbf{r}_i'| \geq 1$. Note that if the chosen reference particle is an electron, then $m_1 = m_e$, $q_1 = -e$ and $a = a_0$ is the Bohr radius. The transformation just proposed is a generalization of the one recently applied to the confined hydrogen atom [2].

It is clear that $\hat{H}_d(\lambda = 0) = \hat{H}_d^0$ is the dimensionless Hamiltonian operator for a system of N free particles in a spherical box of unit radius. Therefore, we can solve the eigenvalue equation $\hat{H}_d^0\varphi^{(0)} = \epsilon^{(0)}\varphi^{(0)}$ exactly in terms of products of spherical harmonics and Bessel functions [1–5]. It may also be necessary to consider the permutational symmetry of the wavefunction and add the corresponding spin factors [1].

For concreteness, let us consider the He atom. We assume that the particles 1 and 2 are the electrons and the remaining one is the nucleus; that is to say: $m_1 = m_2 = m_e$ and $m_3 = m_n$. Obviously, in such a case $m'_1 = m'_2 = 1$, $m'_3 = m_n/m_e$ and the unperturbed wavefunction for the ground state is

$$\varphi^{(0)}(r'_1, r'_2, r'_3) = 2\frac{\sin(\pi r'_1)}{r'_1}\frac{\sin(\pi r'_2)}{r'_2}\frac{\sin(\pi r'_3)}{r'_3}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{5}$$

Note that the present model accounts for the motion of the nucleus and that the nuclear factor $\sin(\pi r'_3)/r'_3$ does not appear if this particle is clamped at the center of the box [1,5].

If we apply straightforward Rayleigh–Schrödinger perturbation theory we obtain the well–known expansions

$$\epsilon = \sum_{j=0}^{\infty} \epsilon^{(j)} \lambda^j, \ \varphi = \sum_{j=0}^{\infty} \varphi^{(j)} \lambda^j \tag{6}$$

In particular, for the energy we have

$$E = \frac{\hbar^2}{m_1 a^2}\left[\frac{\epsilon^{(0)}}{\lambda^2} + \frac{\epsilon^{(1)}}{\lambda} + \epsilon^{(2)} + \ldots\right] \tag{7}$$

that is a generalization of the result derived by Laughlin [4] and discussed by Laughlin and Chu [5] and Montgomery et al. [1]. Note that present Eqs. (6) and (7) apply to the most general case of a system of N particles (3).

If both φ and $\varphi^{(0)}$ are normalized to unity we can easily prove that

$$\left|\langle\varphi|\ \varphi^{(0)}\rangle\right| \leq 1, \ \lim_{\lambda\to 0}\left|\langle\varphi|\ \varphi^{(0)}\rangle\right| = 1 \tag{8}$$

which clearly account for the behaviour of the overlap integral in Fig. 1 of Montgomery et al. [1] for the particular case of the He^+. We stress that Eq. (8) applies to the general case of N particles.

As an illustrative example we calculate the energy of the helium atom corrected through first order. When the nucleus is clamped at the origin we have [1,5]

$$\frac{\epsilon(\lambda)}{\lambda^2} = \frac{9.8696044}{\lambda^2} - \frac{7.9645404}{\lambda} \tag{9}$$

On the other hand, when the nucleus moves the result is

$$\frac{\epsilon(\lambda)}{\lambda^2} = \frac{9.870280744}{\lambda^2} - \frac{5.358219501}{\lambda} \tag{10}$$

where we have chosen $m_n = 7296.300\, m_e$. It is worth noting that the effect of the nuclear motion is more noticeable on the average potential energy than on the average kinetic one in agreement with previous results for the hydrogen atom [2].

3 Conclusions

We have shown that converting the Schrödinger equation into a dimensionless eigenvalue one greatly facilitates the application of perturbation theory to strongly confined systems. In particular this approach clearly shows that the interaction between the particles becomes negligible as the confinement increases. In this way we could provide a suitable mathematical basis for recent numerical calculations on the He atom with a nucleus clamped at origin. Eq. (8) not only explains the behavior of the overlap integral calculated by Montgomery et al. [1] but also reveals that the same kind of curve should be expected for any system of particles confined in a spherical box.

We have also shown that the effect of the nuclear motion on the kinetic energy of the confined atom is not as important as its effect on the average Coulomb interactions. The reason is that the energy of the confined atom changes markedly with the location of the clamped nucleus within the box and is minimum at the center [6]. Therefore, when the nucleus is allowed to move we expect a sort of average contribution to the potential energy from all the possible locations inside the box. In addition to it, the energy of the clamped-nucleus atom (9) is smaller than the moving-nucleus one (10) for all values of R_c at least in the strong-coupling regime.

References

1. H.E. Montgomery Jr, N. Aquino, A. Flores-Riveros, Phys. Lett. A **374**, 2044 (2010)
2. F.M. Fernández, Eur. J. Phys. **31**, 285 (2010)
3. F.M. Fernández, *Introduction to Perturbation Theory in Quantum Mechanics* (CRC Press, Boca Raton, 2001)
4. C. Laughlin, Adv. Quantum Chem. **57**, 203 (2009)
5. C. Laughlin, S.-I. Chu, J. Phys. A **42**, 265004 (11 pp.) (2009)
6. J.L. Marín, R. Rosas, A. Uribe, Am. J. Phys. **63**, 460 (1995)