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Critical radius and dipole polarizability for a confined system*

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The analytical transfer matrix method (ATMM) is applied to calculating the critical radius r_c and the dipole polarizability α_d in two confined systems: the hydrogen atom and the Hulthén potential. We find that there exists a linear relation between $r_c^{1/2}$ and the quantum number n_r for a fixed angular quantum number l, moreover, the three bounds of α_d (α_d^K, α_d^B, α_d^U) satisfy an inequality: $\alpha_d^K \leq \alpha_d^B \leq \alpha_d^U$. A comparison between the ATMM, the exact numerical analysis, and the variational wavefunctions shows that our method works very well in the systems.

Keywords: ATMM, confined system, critical radius, dipole polarizability
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1. Introduction

A number of properties of confined systems have been investigated over the years.[1−6] Sommerfeld and Welker[7] carried out a detailed research on the binding energy in a confined hydrogen atom. They found that there was a critical radius r_c at which the binding energy became zero when the confined radius r_0 decreased. They also found that the energy of this system was positive when $r_0 < r_c$, where r_c is relevant to the partition function of atom and to the pressure ionization of the ground state and excited states of atom.[8] Dingle,[9] Boeyens[10] and Varshni[8] calculated the r_c values by using various methods for a confined hydrogen atom.

What is more, dipole polarizability α_d is a useful quantity in the theoretical description of long-range forces in weakly interaction systems and of optical properties of materials.[11,12] Experimental data are available for some alkali and alkaline-earth metals.[13,14] Theoretical approaches to the calculation of dipole polarizability are based on the coupled Hartree–Fock method[15,16] or the finite perturbation method[17] or the variational wavefunction method.[18]

In this paper, we extend the analytical transfer matrix method (ATMM)[19] to computing both the critical radius r_c and dipole polarizability α_d for the confined hydrogen atom and the confined Hulthén potential. Our results are in good agreement with calculations from the exact numeration;[8,18] however, those from the variational wavefunction have varying degree of errors.

2. Analytical transfer matrix method

In a central force potential $V(r)$, the radial wavefunction $\chi(r)$ satisfies the Schrödinger equation

$$\frac{\mathrm{d}^2\chi(r)}{\mathrm{d}r^2} + \frac{2m}{\hbar^2}[E - V_{\mathrm{eff}}(r)]\chi(r) = 0. \qquad (1)$$

For a spherical potential, the effective potential is

$$V_{\mathrm{eff}}(r) = V(r) + \hbar^2 l(l+1)/(2mr^2). \qquad (2)$$

Now we introduce the ATMM[19,20] and apply it to a particle that is confined in a sharp potential with

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radius r_0. So the boundary conditions of the wave-function for this system are changed into $\chi(0) = 0$, and $\chi(r_0) = 0$.

The region of space can be divided into three parts:

Part 1: $r_c \le r < r_{t_1}$, where $E < V_{\rm eff}(r)$;

Part 2: $r_{t_1} \le r \le r_{t_2}$, where $E > V_{\rm eff}(r)$;

Part 3: $r_{t_2} < r \le r_d$, where $E < V_{\rm eff}(r)$.

Here r_{t_1} and r_{t_2} are the classical turning points; $V_{\rm eff}(r_c) \to \infty$, and $V_{\rm eff}(r_d) \to \infty$. Three regions are divided into l, w and n section layers respectively with an equal width of d and the ATMM is applied to each region. As the division becomes finer and finer, the potential in each layer can be regarded as constant.

After some simple algebra calculation based on Ref.[19], the quantization condition is

$$\int_{r_{t_1}}^{r_{t_2}} k\,{\rm d}r + \phi(s) = n_r\pi + \arctan\left(\frac{p_l}{k_{l+1}}\right) + \arctan\left(\frac{p_{l+w+1}}{k_{l+w}}\right), \quad n_r = 0, 1, 2, \ldots, \tag{3}$$

where

$$k_j = \sqrt{2m[E - V_{\rm eff}(r)]}/\hbar, \quad j = l+1, l+2, ..., l+w; \tag{4}$$

$$p_j = \sqrt{2m[V_{\rm eff}(r) - E]}/\hbar, \quad j = 1, 2, ..., l, \quad \text{or} \quad = l+w+1, l+w+2, ..., l+w+n, \tag{5}$$

n_r is the quantum number, $\arctan(p_l/k_{l+1})$ and $\arctan(p_{l+w+1}/k_{l+w})$ are the half phase shifts at the turning points. $\phi(s)$ is the phase contribution due to the reflections of the sub-waves and when we define $P(r) = -u'(r)/u(r)$, it can be written as[20]

$$\phi(s) = \int_{r_{t_1}}^{r_{t_2}} \left(-k'\frac{P}{P'}\right){\rm d}r. \tag{6}$$

The half phase shifts at the turning points are equal to $\pi/2$ and then Eq.(3) can be rewritten as

$$\int_{r_{t_1}}^{r_{t_2}} (k - k'\frac{P}{P'}){\rm d}r = (n_r + 1)\pi, \quad n_r = 0, 1, 2, \ldots. \tag{7}$$

According to the value of the confinement parameter r_0, we obtain two sets of quantization rules. The above analysis is relevant to relatively large confinement that contains two turning points, namely, $r_0 > r_{t_2}$. When the confinement is very small and includes only one turning point, i.e. $r_{t_1} < r_0 < r_{t_2}$, the region of space is only divided into two segments. According to similar analysis and deducing, the quantization rule is

$$\int_{r_{t_1}}^{r_0} \left(k - k'\frac{P}{P'}\right){\rm d}r = \left(n_r + \frac{1}{2}\right)\pi, \quad n_r = 0, 1, 2, \ldots. \tag{8}$$

Table 1. Critical radii r_c obtained by using the ATMM, the exact numerical method, and the variational equation for $l = 1$. Radii are in units of Bohr radius.

n_r	Exact	ATMM	VAR
2	5.0883	5.0883	5.3193
3	11.910	11.910	11.926
4	21.174	21.174	21.121
5	32.900	32.900	32.868
6	47.091	47.091	47.128
7	63.747	63.747	63.852
8	82.871	82.871	82.991
9	104.46	104.46	104.49
10	128.52	128.52	128.27

3. Critical radius r_c

For the hydrogen atom and the Hulthén potential, we have $V(r) = -1/r$ and $V(r) = -\delta {\rm e}^{-\delta r}/(1 - {\rm e}^{-\delta r})$ respectively.

We set $\hbar = m = e = 1$ for simplicity. When $r_0 > r_{t_2}$, namely, the confinement is so large that it includes two turning points, the three-dimensional quantization rule for the confined system[21] is expressed by Eq.(7), where $k = \sqrt{2[E - V_{\rm eff}(r)]}$ and P is determined from the Riccati equation ${\rm d}P/{\rm d}r = P^2 + k^2$. When $r_{t_1} < r_0 < r_{t_2}$, namely, the confinement is very small and includes only one turning point, the quantization rule is changed to that expressed by Eq.(8).

It is well known that when $r_0 = r_c$, $E = 0$. In order to compute r_c, we let $E = 0$ in Eq.(7) or Eq.(8), then obtain the corresponding results for $l = 1$ in Table 1 for the hydrogen atom. A comparison between the ATMM, the exact numerical method, and the variational equation shows that the ATMM is accurate, whereas the variational equation shows some deviations from the exact numeration.

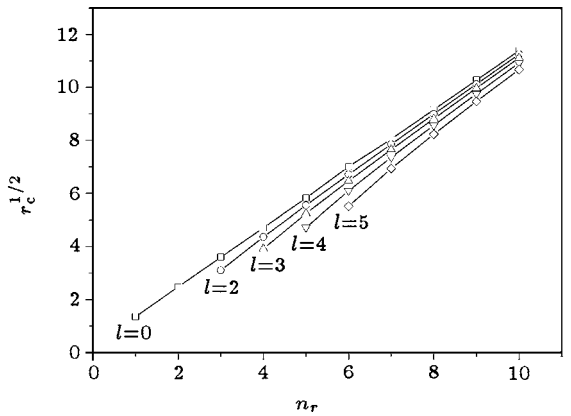


Fig.1. Square root of r_c against n_r for $l = 0, 2, 3, 4, 5$.

Figure 1 shows $r_c^{1/2}$ against n_r for $l = 0, 2, 3, 4, 5$. The relation between $r_c^{1/2}$ and n_r is nearly linear. In addition, we obtain the following values of r_c for the confined Hulthé potential by using the ATMM:

For the $1s$ state: $r_c = 1.894$ when $\delta = 0.1$, and $r_c = 1.958$ when $\delta = 0.2$; for the $2p$ state: $r_c = 5.826$ when $\delta = 0.1$, and $r_c = 7.043$ when $\delta = 0.2$.

4. Dipole polarizability α_d

We should first calculate the energies in these confined systems before obtaining the dipole polarizability.

Energies are calculated with the quantization rules expressed by Eqs.(7) and (8) for the confined hydrogen atom. The results are shown in Table 2 for various values of the confined radius r_0. The exact energies are calculated by using the method of Goldman and Joslin under the condition that the wavefunction is zero at r_0.[22] There is very good agreement between the energies obtained from the ATMM and those of the exact numeration.

Table 2. Energy eigenvalues for $1s$ and $2p$ states obtained by the ATMM, the exact numerical method, and the variational wavefunction for the confined hydrogen atom.

r_0	$1s$			$2p$		
	Exact	ATMM	VAR	Exact	ATMM	VAR
0.4	24.634	24.634	24.651	58.448	58.448	58.523
0.6	9.528	9.528	9.534	24.937	24.937	24.968
0.8	4.544	4.544	4.545	13.440	13.440	13.455
1.0	2.374	2.374	2.375	8.223	8.223	8.232
1.4	0.647	0.647	0.647	3.807	3.807	3.817
1.6	0.271	0.271	0.271	2.765	2.765	2.767
1.8	0.033	0.033	0.033	2.065	2.065	2.067
2.0	–0.125	–0.125	–0.125	1.576	1.576	1.577
2.5	–0.3349	–0.3349	–0.3343	0.852	0.852	0.853
3.0	–0.4240	–0.4240	–0.4225	0.4813	0.4813	0.4815
3.5	–0.4644	–0.4644	–0.4624	0.2712	0.2712	0.2713
4.0	–0.4833	–0.4833	–0.4811	0.1435	0.1435	0.1436
5.0	–0.4964	–0.4964	–0.4947	0.0076	0.0076	0.0076
6.0	–0.4993	–0.4993	–0.4982	–0.0556	–0.0556	–0.0556
7.0	–0.4999	–0.4999	–0.4993	–0.0875	–0.0875	–0.0874

Dipole polarizability, which describes the lowest-order response to an electric field,[18] is the most important electric property of atoms and molecules.[23] Theoretical calculations of this property may be very helpful, especially when no experimental results are available. Kirkwood proposed the expression for the polarizability for single-electron atoms in free space,[24]

$$\alpha_d^K = \frac{4\langle r^2\rangle^2}{9}. \tag{9}$$

Compared with Kirkwood's work, Buckingham took into account high-order terms[25] to obtain Eq.(10) that could give the better outcome. In Ref.[26], Unsold proposed an upper bound to the exact polarizability,

$$\alpha_d^B = \frac{2}{3}\left[\frac{6\langle r^2\rangle^3 + 3\langle r^3\rangle^2 - 8\langle r\rangle\langle r^2\rangle\langle r^3\rangle}{9\langle r^2\rangle - 8\langle r\rangle^2}\right], \tag{10}$$

$$\alpha_d^U = \frac{2}{3}\frac{\langle r^2\rangle}{E_{2p} - E_{1s}}. \tag{11}$$

These expressions have been applied to the confined system.[6–27] In order to obtain α_d^K, α_d^B, and α_d^U, we need to calculate the expectation values $\langle r^n\rangle$ by using the equation:

$$\langle r^n\rangle = \frac{\int_0^{r_0} \chi_{\text{state}} r^n \chi_{\text{state}}}{\int_0^{r_0} \chi_{\text{state}}\chi_{\text{state}}}, \quad n = 1, 2, 3. \tag{12}$$

We can easily acquire the wavefunction based on the following equation, with the energies determined,

$$\begin{bmatrix} \chi(r) \\ \chi'(r) \end{bmatrix} = M \begin{bmatrix} 1 \\ -P(r_0) \end{bmatrix},$$

$$M = M_{r+d} M_{r+2d} \cdots M_{r+id} \cdots M_{r_0-d}, \qquad (13)$$

where M is the analytical matrix the same as that in Ref.[28], and d is the width of the layers.

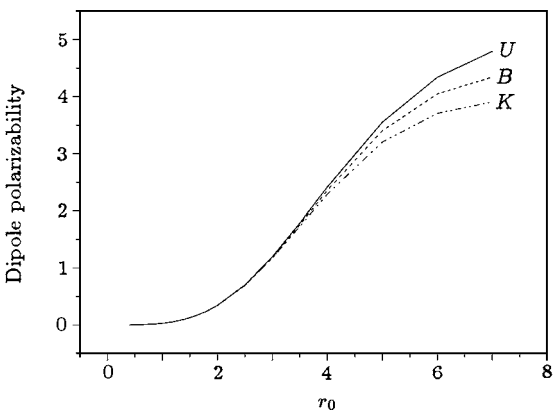


Fig.2. The dipole polarizability of the confined hydrogen atom as a function of r_0 in atomic units. The solid line is for $\alpha_{\rm d}^U$, short dash line is for $\alpha_{\rm d}^B$, dash dot dot line is for $\alpha_{\rm d}^K$.

Using Eq.(12), the values $\langle r\rangle$, $\langle r^2\rangle$, $\langle r^3\rangle$ in the $1s$ state for the confined hydrogen atom are shown in Table 3, and the corresponding $\alpha_{\rm d}^K$, $\alpha_{\rm d}^B$, and $\alpha_{\rm d}^U$ are shown in Fig.2. From the comparison, we find that the results of the ATMM are in good agreement with the exact ones. Figure 2 reveals that $\alpha_{\rm d}^K$, $\alpha_{\rm d}^B$, and $\alpha_{\rm d}^U$ satisfy the relation $\alpha_{\rm d}^K \le \alpha_{\rm d}^B \le \alpha_{\rm d}^U$, which is the same as the conclusion in Ref.[6]. Applying the same method to the confined Hulthén potential, we obtain the same conclusion $\alpha_{\rm d}^B \ge \alpha_{\rm d}^K$ as seen from Fig.3.

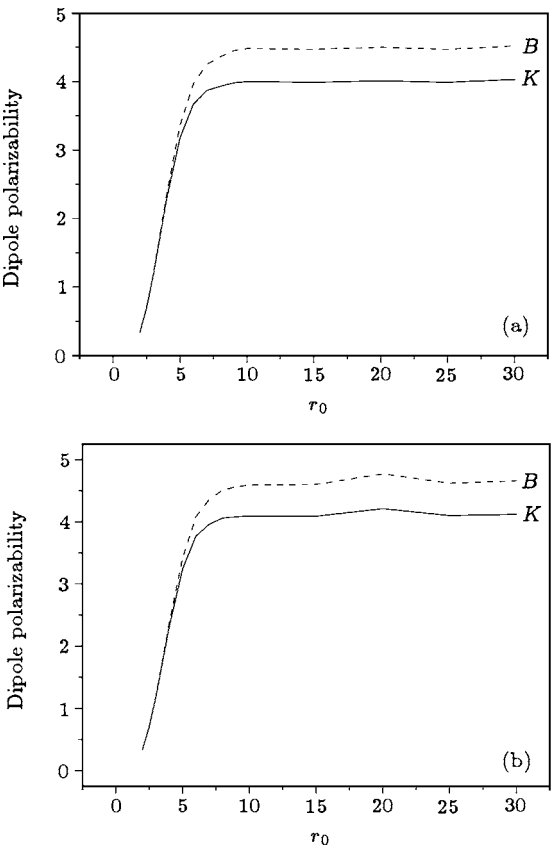


Fig.3. (a) Dipole polarizability of the confined Hulthén potential against r_0 for (a) $\delta = 0.1$, (b) $\delta = 0.2$. $\alpha_{\rm d}^B$ is shown by solid curve while $\alpha_{\rm d}^K$ by the dashed one.

Table 3. The radial expectation values in the 1s and 2p states as a function of the confined radius. Atomic units are used.

r_0	$\langle r\rangle_{\rm exact}$	$\langle r\rangle_{\rm ATMM}$	$\langle r^2\rangle_{\rm exact}$	$\langle r^2\rangle_{\rm ATMM}$	$\langle r^3\rangle_{\rm exact}$	$\langle r^3\rangle_{\rm ATMM}$
0.4	0.19525	0.19525	0.04343	0.04343	0.01057	0.01057
0.6	0.28907	0.28907	0.09559	0.09559	0.03467	0.03467
0.8	0.38015	0.38015	0.16604	0.16604	0.07974	0.07974
1.0	0.46832	0.46832	0.25313	0.25313	0.15087	0.15087
1.2	0.55340	0.55340	0.35514	0.35514	0.25207	0.25207
1.4	0.63521	0.63521	0.47025	0.47025	0.38626	0.38626
1.6	0.71359	0.71359	0.59656	0.59656	0.55520	0.55520
1.8	0.78836	0.78836	0.73209	0.73209	0.75949	0.75949
2.0	0.85935	0.85935	0.87482	0.87482	0.99859	0.99859
2.5	1.01939	1.01939	1.24959	1.24959	1.73502	1.73502
3.0	1.15321	1.15321	1.62477	1.62477	2.62219	2.62219
3.5	1.26028	1.26028	1.97206	1.97206	3.57801	3.57801
4.0	1.34171	1.34171	2.27031	2.27031	4.51102	4.51102
5.0	1.44003	1.44003	2.68497	2.68497	6.02323	6.02323
6.0	1.48091	1.48091	2.88743	2.88743	6.90220	6.90220
7.0	1.49473	1.49473	2.96553	2.96553	7.29466	7.29466

5. Conclusions and discussion

In this work, we have extended the ATMM to computing the critical radius and dipole polarizability for the confined hydrogen atom and the confined Hulthén potential. According to the comparison between the ATMM and the exact numerical calculation, our method is efficient and accurate. Based on the results from our method, we obtain the following conclusions: the relation between $r_c^{1/2}$ and quantum number n_r is linear and when $r < r_c$, the energy of this system is positive, otherwise, it is negative; three values of α_d for α_d^K, α_d^B, α_d^U satisfy the inequality $\alpha_d^K \leq \alpha_d^B \leq \alpha_d^U$, which is the same as the conclusion in Ref.[6].

The ATMM is an exact method of determining r_c and α_d for the confined potentials. It is the first attempt for us to apply the ATMM to the investigation of the properties of such systems. We look forward to finding more properties in the context of the confined potentials by using our method.

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