Orthogonality criteria for singular states and the nonexistence of stationary states with even parity for the one-dimensional hydrogen atom

Dai Xianxi*
Department of Physics, Fudan University, Shanghai 200433, People's Republic of China†
and Texas Center of Superconductivity, University of Houston, Houston, Texas 77204-5932

Jixin Dai
Department of Physics, Fudan University, Shanghai 200433, People's Republic of China
and Department of Chemistry, New York University, 31 Washington Place, New York, New York 10003†

Jiqiong Dai
Department of Chemistry, New York University, 31 Washington Place, New York, New York 10003
and Department of Chemistry and The James Franck Institute, University of Chicago, Chicago, Illinois 60637†
(Received 27 August 1996)

With the aid of two linearly independent Whittaker functions, Loudon obtained the solutions with even and odd parity for the one-dimensional hydrogen atom. Applying the Schwarz inequality, Andrews made an objection to Loudon's "ground state." Either solving the problem in the momentum representation or basing our work on the theory of singular integral equations, we have proved that these solutions with even parity do not exist. Due to its importance related to the nondegeneracy theorem and to the study of the exciton and Wigner crystal (by electron gas above the helium surface), we have reexamined this problem in the coordinate representation by means of the orthogonality criterion for singular states and the natural connection condition of the wave function's derivatives. We have proved again that all these eigenstates with even parity do not exist. This result is consistent with that of exact solutions in the momentum representation and in the integral equation method canceling divergence. This study not only emphasized the importance of the orthogonality criterion but also generalized its application, including the singular states with poles, essential singular points, phase angle uncertainty, and the logarithmic singularity of derivatives. [S1050-2947(97)03004-7]

PACS number(s): 03.65.Ge, 71.35.−y, 02.90.+p

I. INTRODUCTION

For the stationary state problem of the one-dimensional hydrogen atom (1D H atom), the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)-\frac{Ze^2}{|x|}\psi(x)=E\psi(x)\quad(-\infty<x<\infty),\tag{1}$$

which has attracted a great deal of interest [1–5]. This interest occurs because there are some obvious discrepancies between theory and the conclusions, which may involve several criteria determining singular state solutions in quantum mechanics. Also, the study of the exciton model (including one dimensional) is related to the theory of high temperature superconductivity [6], semiconductors [7,8], and polymers [9–12]. On the other hand, in experiments, scientists are interested in the Wigner crystal [13,14]. These experiments have been carried out on the one-dimensional electron gas at the helium surface. Essentially it can be identified as the 1D H atom problem, due to the existence of an image force. The theoretical discrepancies could be distinguished by experiments. The criterion determining the solution of singular states also can be tested.

It is well known that the wave functions of the 1D H atom and the s states of 3D H atom satisfy the same Schrödinger equation. The only difference between them is the variable x, which can be negative in the 1D H atom.

Introducing the Bohr radius and the following variable transformations,

$$a_0=\frac{\hbar^2}{me^2},\quad \xi=\frac{2x}{\alpha a_0},\quad E=-\frac{\hbar^2}{2ma_0^2\alpha^2},\tag{2}$$

Eq. (1) is transformed into the Whittaker equation [16,17,28],

$$\frac{d^2}{d\xi^2}\psi-\frac{1}{4}\psi+\frac{\alpha}{|\xi|}\psi=0.\tag{3}$$

With the aid of the function transformation $\psi(\xi)=e^{-(1/2)\xi}f(\xi)$, we have

$$\xi f''(\xi)-\xi f'(\xi)+\alpha f(\xi)=0.\tag{4}$$

This is a special case of the Kummer equation:

$$z\frac{d^2y}{dz^2}+(\gamma-z)\frac{dy}{dz}-\alpha y=0.\tag{5}$$

Usually its general solution can be written in the following form:

*Corresponding author.
†Present address.

$$y(z)=AF[-\alpha,\gamma,z]+Bz^{1-\gamma}F[-\alpha-\gamma+1,2-\gamma,z], \tag{6}$$

where F is the confluent hypergeometric function or Kummer function. It is necessary to study the 1D H atom and the s state of the 3D H atom in detail. This is because (it is different from the non-s-state problem in the 3D H atom) the two special solutions in the equation above are equivalent:

$$\lim_{c\to 0}\frac{1}{\Gamma(c)}F(a,c;\xi)=a\xi F(a+1,2,\xi). \tag{7}$$

The important contribution by Loudon to solving this problem was his use of the Whittaker function as the two special solutions of the Whittaker equation, because they are linearly independent under general parameters.

The conclusion of Flugge and Marschall [1] was that there exists a solution set with only odd parity. The conclusions of Loudon were the following: (a) there also exists a set of solutions with even parity simultaneously. (b) They are degenerate with that of odd parity. The binding energy of the ground state is infinite. (c) Then he suggested some improvement on the nondegeneracy theorem for the 1D bound states in quantum mechanics [18]. But using Schwarz's inequality, Andrews [3] proved that Loudon's ground state ψ_0 would be orthogonal with all quadratic integrable wave functions and would make no contribution to the completeness, and could not be observable. Furthermore, Andrews questioned the existence of Loudon's ground state but he did not make any comment on the other states with even parity.

Recently Zhao [4] discussed the nondegeneracy theorem and suggested the condition of nondegeneracy theorem breaking. He also cited Loudon's even solutions as the example of nondegeneracy breaking.

Fortunately, we are interested in the potentials that are singular in the momentum space. Taking the electron above the helium surface as an example, we exactly solved the 1D H atom problem in the momentum space and investigated the momentum representation of the image potential (with divergence in momentum space) [15]. We suggested the criterion eliminating divergence (in momentum space). We proved that the even states cannot satisfy the criterion eliminating the divergence and must be rejected. From the study in momentum space, our conclusion is that only the odd states can exist.

These discrepancies and arguments involve the fundamental theories and theorem in the quantum mechanics. The Wigner crystal problem is also very interesting in both experiments and theory and could check the validity of the theories as well as test the criterion determining the solution of singular states. We return to the coordinate space to discuss the 1D H atom problem in detail.

II. QUESTION AND GOAL

Not only Flugge and Marschall [1], but also Loudon [2], quantized the energy of the 1D H atom by discussing only the right-half space. Their results are inclusive and open to discussion. From a theoretical point of view, this kind of procedure would appear to be unacceptable, because it can lead to incorrect results. For example, if we change the potential in left-half space to minus linear potential, it is obvious that in the physics and mathematics the particle will flow into left space, and there are no bound states. But, if people quantized the energy in advance according to the study in right-half space, the conclusion must be wrong.

It is very interesting that up to now, to our knowledge, no one has given the energy quantization of the 1D H atom by whole standard conditions in the coordinate space naturally. One of the goals of this paper is to give a natural description in coordinate space and reach a correct conclusion to clarify the arguments and to discuss a general criterion determining the solution with singular states in quantum mechanics.

III. BOUNDARY CONDITION OF SINGULAR POTENTIAL

In quantum mechanics, it is generally believed that when the potential is discontinuous with a finite jump, then the ''smooth connection of the wave function'' (the continuation of the wave function and its derivative) is required. When the potential is divergent, the continuation of the wave function is still required, but the continuation of its derivative is not. The basis of these propositions and the quantitative formulation of the discontinuity of its derivatives must be clarified. This is a key issue.

From a physical point of view, the boundary condition is the manifestation of the field equation at the boundary. Usually that condition is obtained by taking the limit of the integral field equation. The boundary conditions of the Maxwell equation in an electromagnetic field are typical examples. Along this line, we develop the discussion on the boundary condition at the singularity.

If $x=a$ is a singularity of the potential $V(x)$, then $x=a$ can be considered as a boundary (point) of the field equation (such as the Schrödinger equation). The corresponding variation of the derivatives of the wave function can be obtained by the field equation itself:

$$\psi'(a+\epsilon)-\psi'(a-\epsilon)=\frac{2m}{\hbar^2}\int_{a-\epsilon}^{a+\epsilon}[V(x)-E]\psi(x)dx,\quad (\epsilon\to 0^+). \tag{8}$$

The following is clear: (1) When the jump of the potential is finite, the derivative of the wave function is continuous at $x=a$. (2) In the famous 1D many-body problem with a δ-function potential [20], the connection condition of the wave function also satisfies this condition. (3) When the wave function is finite, and the potential $V(x)$ is divergent at $x=a$ but not a δ-function potential, for example, in the 1D H atom case, the condition of Eq. (8) naturally becomes

$$\psi'(0^+)-\psi'(0^-)=\frac{2m}{\hbar^2}\int_{0^-}^{0^+}V(x)\psi(x)dx. \tag{9}$$

This can be considered as an application of the above boundary condition.

IV. THE ORTHOGONALITY CRITERION OF THE SINGULAR STATE OF THE 1D CASE

From our point of view, the even states in the 1D H atom belong to a new kind of singular state, because the derivative of the wave function is discontinuous.

In physics, singular states do exist. Sometimes they are very important and the eigen-function set will sometimes be incomplete without them. The famous ground state of the Dirac equation of a hydrogen atom is also a singular state, which is divergent at the origin.

Due to the importance of singular states in physics, many detailed investigations on singular states and their applications have appeared in the literature [21–25].

In a singular potential problem, usually there are no singular states. It is interesting that some singular states satisfy the equation and are quadratic integrable, but the energy spectrum is continuous. Sometimes they have complex eigenvalues. After detailed investigation, it was found that the character of these states is not orthogonal [21–25].

In traditional quantum mechanics, the orthogonality of the eigenfunction set is a necessary result of the Hermitian operator and is guaranteed by mathematical theorem. But for singular potentials, it is necessary to make suitable adjustments. In order to set up a generalized quantum mechanics framework, including the singular states simultaneously, starting from the requirement of reality of measured probabilities, one needs the orthogonality of the eigenfunction set [22]. According to the criterion of orthogonality, one can judge which singular state can exist and which cannot.

The exact definition of the orthogonality of two states is the following:

$$\int \psi_1^* \psi_2 d\tau = 0, \tag{10}$$

But in the usual cases the calculations are not easy. If ψ_1 and ψ_2 satisfy the equation of motion, the best way to judge the orthogonality is according to the asymptotic behavior at the singularity of the wave functions. We call these criteria the ''orthogonality criteria.''

For the Dirac equation, the orthogonality criterion is obtained as [21,23]

$$\lim_{r\to 0; R\to\infty} q(r)|_r^R = \frac{1}{\hbar c}\delta(E_1 - E_2), \tag{11}$$

where

$$q(r) = \frac{r^2}{E_2 - E_1}[f_1^*(r)g_2(r) - f_2(r)g_1^*(r)]. \tag{12}$$

Making use of this criterion, the authors discussed the hydrogenlike atom with $z > 137$ [21,25], the singular states with essential singularity in the monopole-monopole system [23], also rejected all the singular states (with pole singularity) with complex eigenvalues [25].

In Ref. [24], using the monopole harmonics [26], we obtained the orthogonality criterion for electron-monopole system, especially for so-called ''type III states'':

$$\lim_{r\to 0; R\to\infty} - \frac{i(q/|q|)\hbar c r^2}{E_2 - E_1}\{f_1^*(r)g_2(r) + g_1^*(r)f_2(r)\}|_r^R = \delta(E_1 - E_2). \tag{13}$$

According to this criterion, the phase-angle uncertainty in the relativistic quantum mechanics can be locked in and the same result can be obtained as that obtained by Kazama, Yang, and Goldharber [27] by another method. In Ref. [25], we have discussed the orthogonality criteria in detail and have given some numerical results of the energy level equation, (obtained from the orthogonality criteria) of the hydrogenlike atom (with $z > 137$).

The orthogonality criterion for the 3D Schrödinger equation is [22]

$$\lim_{r\to 0; R\to\infty} - \frac{\hbar^2 r^2}{2m(E_2 - E_1)}[R_1^*(r)R_2'(r) - R_1'^*(r)R_2(r)]|_r^R = \delta(E_1 - E_2). \tag{14}$$

The singular state problem for the following potential is discussed [22]:

$$U(r) = -\frac{\alpha}{r} - \frac{\beta}{r^2}. \tag{15}$$

Now, extend the orthogonality criterion to the 1D situation,

$$\lim_{r\to 0; R\to\infty} Q(x)|_r^R = \delta(E_2 - E_1), \tag{16}$$

where

$$Q(x) = -\frac{\hbar^2}{2m(E_2 - E_1)}[\psi_1^*(x)\psi_2'(x) - \psi_1'^*(x)\psi_2(x)]. \tag{17}$$

This situation is different from that discussed previously (the pole, essential singularity, and phase angle uncertainty). Here, there is a singularity of the derivative of the function. And the singularity is of logarithmic (branch point) singularity.

V. THE EXACT SOLUTION OF THE 1D H ATOM

It is obvious that Eq. (3) is a special case of the Whittaker equation:

$$W'' + \left[-\frac{1}{4} + \frac{k}{z} + \frac{\frac{1}{4} - m^2}{z^2}\right]W = 0. \tag{18}$$

Its two special solutions could be Whittaker functions: $W_{k,m}(z)$ and $W_{-k,m}(z)$. The merit of choosing these Whittaker functions is that they are linearly independent under the general parameters. They have the following asymptotic behavior:

$$W_{\pm k,m}(\pm z) = e^{\pm z/2}(\pm z)^{\pm k}\{1 + O(z^{-1})\}. \tag{19}$$

They can be obtained by the Barnes integral representation [28]. When $2m$ is an integer,

$$W_{k,m}(z)=\frac{(-1)^{2m+1}}{(2m)!\Gamma(\frac{1}{2}-k-m)}\Bigg[e^{-z/2}z^{1/2+m}F[\tfrac{1}{2}+m-k,1+2m,z]\ln(z)+\sum_{n=0}^{\infty}\frac{(\frac{1}{2}-k+m)_n}{n!(1+2m)_n}z^{n+m+1/2}e^{-z/2}\{\psi(\tfrac{1}{2}-k+m+n)-\psi(1+2m+n)-\psi(1+n)\}+(-1)^{2m+1}e^{-z/2}z^{1/2+m}\frac{(2m-1)!(2m)!\Gamma(\frac{1}{2}-k-m)}{\Gamma(\frac{1}{2}-k+m)}\sum_{n=0}^{2m-1}\frac{(\frac{1}{2}-k-m)_n}{n!(1-2m)_n}z^{n-2m}\Bigg], \tag{20}$$

where $(B)_n\equiv\Gamma(B+n)/\Gamma(B)$ and $2m=0,1,2,\ldots.$

Now for the 1D H atom:

$$k=\alpha,z=\xi,m=\tfrac{1}{2},\gamma=1+2m. \tag{21}$$

Then the solution is

$$W_{\alpha,1/2}(\xi)=\frac{e^{-\xi/2}}{\Gamma(-\alpha)}\Bigg\{\xi F[1-\alpha,2,\xi][\ln(\xi)+\psi(1-\alpha)-\psi(2)-\psi(1)]-\frac{1}{\alpha}+\sum_{n=1}^{\infty}\frac{(1-\alpha)_n}{n!(n+1)!}\xi^{n+1}A_n\Bigg\}, \tag{22}$$

where

$$A_n=\sum_{l=0}^{n-1}\left[\frac{1}{1-\alpha+l}-\frac{1}{2+l}-\frac{1}{1+l}\right]. \tag{23}$$

This is the same result as that found by Loudon, using the Frobenius method.

In the positive half-space, considering the asymptotic behavior of Eq. (19), the quadratic integrable condition of the bound state rejects another special solution. Due to the inversion symmetry of the Hamiltonian, we can search for a common eigenfunction set of energy and parity. We have

$$\psi_o(x)=\begin{cases}W_{\alpha,1/2}(\xi) & (x>0)\\ -W_{\alpha,1/2}(-\xi) & (x<0),\end{cases} \tag{24}$$

$$\psi_e(x)=\begin{cases}W_{\alpha,1/2}(\xi) & (x>0)\\ W_{\alpha,1/2}(-\xi) & (x<0).\end{cases} \tag{25}$$

Considering $W_{\alpha,1/2}(\xi)$ has derivative logarithmic singularity at $x=0$, Loudon generally rejects this kind of function, except α equal to an integer [2]. Then even if one considers only the right half-space, the energy is quantized already. This conclusion is similar to that of Ref. [1].

We have a different opinion: (1) This procedure of energy quantization is not acceptable in the theory, because the potential on the left-half space surely can have an effect on the energy levels. (2) Generally rejecting the solutions in which the derivatives having logarithmic singularity is not correct, since the Dirac ground state of the H atom, the order of singularity (pole) is higher. According to the quadratic integrability, Dirac accepted this ground state. Physicists eventually accepted this important (singular) state. If based on the same standard (quadratic integrability), these Whittaker functions also should be accepted as a possible wave function. But as time has passed, it has been found that many singular states, having complex eigenvalues, are quadratic integrable. Besides, there are some singular states, having continuous (real) eigenvalues, that are also quadratic integrable. So up to now, in the theoretical study of the 1D H atom, the energy quantization problem still has not been solved.

Our point of view is that the orthogonality of the eigenfunction set is the requirement of the reality of measured probability [22]. This is a physical and natural requirement and must be satisfied by all the eigenfunction sets, for both regular and singular states. The regular states naturally satisfy the orthogonality criterion. For singular states, the situation is totally different. The criterion is especially significant for singular states. The orthogonality criterion lets us sieve the function class, which satisfies the (wave) Schrödinger equation: the physical states are accepted and all the singular states not satisfying the orthogonality criterion are rejected. So, just as in other standard conditions, the orthogonality criterion is a physical requirement. It is this requirement that can lead to the energy quantization for many singular states.

Considering that the wave function of the bound state turns to zero at infinity, the orthogonality criterion of 1D H atom can be simplified as

$$[\psi_1^*(x)\psi_2'(x)-\psi_1'^*(x)\psi_2(x)]\big|_{0^-}^{0^+}=0. \tag{26}$$

Because even and odd functions are orthogonal to each other, we only need consider ψ_1 and ψ_2; both are even or both are odd. Then $Q(x)$ are always odd functions.

We need not take the limit value of α in advance. Starting from the general solution (22), we keep all nonzero terms. Especially notice the logarithmic term, which could lead to the derivative singularity

$$W_{\alpha,1/2}(0^+)=\frac{1}{\Gamma(1-\alpha)}; \tag{27}$$

$$\frac{d}{dx}W_{\alpha,1/2}(\xi)|_{\xi\to 0^+}=\frac{2}{\alpha a_0\Gamma(-\alpha)}\left\{\ln(\xi)+\psi(1-\alpha)-\psi(2)-\psi(1)+1+\frac{1}{2\alpha}\right\}. \tag{28}$$

1. When both ψ_1 and ψ_2 are odd functions:

$$\int_{-\infty}^{\infty}\psi_1^*\psi_2 dx=\frac{2\hbar^2}{ma_0[E_2-E_1]\Gamma(1-\alpha_1)\Gamma(1-\alpha_2)}\left\{\ln\left(\frac{\alpha_1}{\alpha_2}\right)+\psi(1-\alpha_2)-\psi(1-\alpha_1)+\frac{1}{2\alpha_2}-\frac{1}{2\alpha_1}\right\}. \tag{29}$$

Note especially that the logarithmic derivative and logarithmic uncertainty at the coordinate origin have already disappeared. Then from the orthogonality criterion we obtain the equation for determining the energy levels:

$$I_{12}=\frac{1}{\Gamma(1-\alpha_1)\Gamma(1-\alpha_2)}\left\{\ln\left(\frac{\alpha_1}{\alpha_2}\right)+\psi(1-\alpha_2)-\psi(1-\alpha_1)+\frac{1}{2\alpha_2}-\frac{1}{2\alpha_1}\right\}=0. \tag{30}$$

It is not easy to solve this kind of equation, because it has pairwise orthogonal relations. Generally speaking, for any fixed α_1, to obtain the totality of α_2: $\{\alpha_2\}$, we need to solve $N(N-1)/2$ equations. Notice that, because the orthogonal criterion must be satisfied by every two eigenstates, the obtained totality $\{\alpha_1\}$ must be the same as the totality of $\{\alpha_2\}$. In other words, we cannot obtain such a result, given α_1, to solve the equations and get a set $\{\alpha_2\}$, but α_1 does not belong to $\{\alpha_2\}$. In mathematics, this causes many difficulties. Sometimes these serious limitations provide a significant advantage. For our case, it is obvious that satisfying all the pairwise orthogonal relations, the exact solution only can be the totality of natural numbers:

$$\alpha=1,2,3,\ldots. \tag{31}$$

Then we obtain a branch of the discrete energy spectrum:

$$E_n=-\frac{\hbar^2}{2\,ma_0^2n^2}\quad(n=1,2,3,\ldots) \tag{32}$$

When $\alpha=n$ is an integer, the Whittaker functions become associate Laguerre polynomials:

$$\lim_{\alpha\to n}W_{\alpha,1/2}(\xi)=\frac{(-1)^n}{n}\xi e^{-\xi/2}L_n^1(\xi). \tag{33}$$

At the same time, these functions satisfy all the connection conditions of the wave function and its derivatives:

$$\psi(0^+)=\psi(0^-). \tag{34}$$

$$\psi'(0^+)-\psi'(0^-)=\frac{2m}{\hbar^2}\int_{0^-}^{0^+}V(x)\psi(x)dx=0. \tag{35}$$

Then we obtain the exact eigenfunction with odd parity:

$$\psi(x)=\begin{cases}N_n\xi e^{-\xi/2}L_n^1(\xi) & (x\geq 0)\\ N_n\xi e^{\xi/2}L_n^1(-\xi) & (x\leq 0)\end{cases} \tag{36}$$

2. When both ψ_1 and ψ_2 are even functions:

Notice that in this case, $Q(x)$ is still an odd function. We obtain the same orthogonality expression and the equation determining energy level (30). And it gives exactly the same α and energy level (32). But the wave function has the following form:

$$\psi(x)=\begin{cases}N_n\xi e^{-\xi/2}L_n^1(\xi) & (x\geq 0)\\ -N_n\xi e^{\xi/2}L_n^1(-\xi) & (x\leq 0).\end{cases} \tag{37}$$

All these functions satisfy the continuity condition of the wave function:

$$\psi(0^+)=\psi(0^-), \tag{38}$$

but their derivatives do not satisfy the connection condition (9) because

$$\psi'(0^+)-\psi'(0^-)=4\frac{(-1)^n(n-1)!}{a_0} \tag{39}$$

and

$$\frac{2m}{\hbar^2}\int_{0^-}^{0^+}V(x)\psi(x)dx\neq\psi'(0^+)-\psi'(0^-). \tag{40}$$

Then we can definitely reject all these states with even parity. It also eliminates the counterexample of the nondegeneracy theorem, which has been proposed by Loudon [2] and cited by Zhao [4].

VI. ON THE ARGUMENT BETWEEN ANDREWS AND LOUDON ON THE GROUND STATE

One of the most interesting states is the state with $\alpha\to 0$. This is suggested by Loudon as the ground state. It has infinite binding energy and $E\to-\infty$. The logarithmic singularity of its derivative has already disappeared. According to Eq. (22),

$$\psi_0=W_{\alpha,1/2}(\xi)=e^{-\xi/2}\quad(\alpha\to 0). \tag{41}$$

This solution can be derived also from Eq. (3) directly. The odd state, consisting of this expression, satisfies the derivative connection condition (35) obviously. But the wave function has discontinuity at the origin. For the even state, consisting of the expression (41), the wave function is continuous. It is understandable that some people think that this state will possibly be a physical state. But this even state does not satisfy the derivative connection condition (35), because

$$\psi'(0^+)-\psi'(0^-)=-\frac{2}{\alpha a_0}.$$

$$\frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon}V(x)\psi(x)dx=\lim_{\epsilon_0/\epsilon\to 0^+}\frac{4m}{\hbar^2}\int_{\epsilon_0}^{\epsilon}V(x)\psi(x)dx$$
$$=-\frac{4me^2}{\hbar^2}\ln\left(\frac{\epsilon}{\epsilon_0}\right). \quad (42)$$

The latter integral is divergent and α independent. There is no definite reason to think that these two expressions are equal. But one can argue that when $\alpha\to 0$, both expressions turn to $-\infty$. So the connection condition is not strong enough to reject Loudon's ''ground state.'' And for the s-state problem of the 3D H atom, there also exists a Loudon ground-state problem.

According to the Schwarz inequality, Andrews [3] proved that the scalar product between ψ_0 and quadratic integrable states ψ vanishes. We can further prove that $\psi(x)$ also can be any finite wave function:

$$\left|\int_0^{\infty}\psi_0(x)\psi(x)dx\right|<|\psi|_{\max}\int_0^{\infty}\psi_0(x)dx=|\psi|_{\max}\sqrt{\alpha a_0}\to 0. \quad (43)$$

Andrews claimed that (a) ψ_0 is not required for completeness in the expansion of quadratic integrable functions; (b) ψ_0 is not observable.

However, we do not think that the conclusions are completely true, because the binding energy of ψ_0 is infinite. As long as ψ_0 does exist, all the 1D hydrogen atoms will stay in this ''ground state'' and could never be excited. All the other (excited) states will be not observable. But, in fact, other states surely have been observed. This requires that the fundamental theory of quantum mechanics must propose some significant reasons to reject Loudon's ''ground state.''

According to our studies, we found the following: (1) Andrews has not proved whether $\psi_0(x)$ is orthogonal with other eigenstates in the meaning of quantum mechanics, because the scalar product in Eq. (43) vanishes only due to the infinite binding energy, but not because the sign of the product $\psi_0\psi$ changes alternatively. (2) The orthogonal relation in quantum mechanics,

$$\int_{-\infty}^{\infty}\psi_1^*(x)\psi_2(x)dx=\delta(E_1-E_2), \quad (44)$$

not only specifies the zero scaler product for $E_1\neq E_2$, but also completely fixes the energy dependence. For example, if we time it by any integer function $I(E_1-E_2)$, the result must be zero:

$$I(E_1-E_2)\int_{-\infty}^{\infty}\psi_1^*(x)\psi_2(x)dx=0 \quad (E_1\neq E_2). \quad (45)$$

It is obvious that Eq. (45) cannot be guaranteed by Eq. (43). [For instance, $I(E_1-E_2)=E_1-E_2$.]

Now let us check the orthogonality criterion. According to Eqs. (41) and (33),

$$Q(0^+)\sim\psi_0^*(0^+)\psi_n'(0^+)-\psi_0'^*(0^+)\psi_n(0^+)=\psi_n'(0^+)$$
$$=\frac{2}{n^2a_0}(-1)^nL_n^1(0)\neq 0. \quad (46)$$

This means that neither even nor odd states with $\alpha\to 0$ could exist. The conclusion is that the essential reason for the nonexistence of these states is their nonorthogonality with other eigenstates. This conclusion is consistent with that obtained by Andrews by Schwarz's inequality, but the foundation is totally different.

VII. *s* STATE OF 3D HYDROGEN ATOM AND OTHERS

In order to explain the correctness of the orthogonality criteria and its application, we consider the following potential:

$$V(x)=-\frac{\alpha_0}{r}-\frac{\beta}{r^2}. \quad (47)$$

The radial wave functions of the 3D Schrödinger equation $u(r)\equiv rR(r)$ satisfy the following equation:

$$u''(r)+\left[\frac{2mE}{\hbar^2}+\frac{2m\alpha_0}{\hbar^2 r}+\frac{2m\beta/\hbar^2-l(l+1)}{r^2}\right]u(r)=0. \quad (48)$$

One can transform it into a confluent hypergeometric equation by a suitable transformation. Denote

$$\Gamma=\frac{2m\beta}{\hbar^2}-l(l+1)\neq 0. \quad (49)$$

It is easy to express the general solution by a linear combination of two linear independent special solutions. The general solution with $\Gamma=0$ is often obtained by the same method. But in fact, in this case, these two special solutions are the same. So we meet the same problem as previously mentioned. As described before, we can express the general solutions (with $\Gamma=0$) by two Whittaker functions (as Loudon has done). Repeating the previous discussion, denoting $\alpha_0=ze^2$, the main difference is the limitation on the variable $(r\geqslant 0)$. We can also judge which solutions are physical by the almost the same orthogonality criterion:

$$\int_0^{\infty}\int_0^{\pi}\int_0^{2\pi}\psi_1^*\psi_2 r^2dr\ \sin(\theta)d\theta d\phi=-Q(0^+)=0, \quad (50)$$

where

$$Q(r) = -\frac{\hbar^2 r^2}{2m[E_2 - E_1]}[R_1^*(r)R_2'(r) - R_2(r)R_1'^*(r)]. \tag{51}$$

When $u(r)$ are the Whittaker functions as expressed in Eq. (22), the orthogonality criterion becomes an equation determining the energy levels:

$$\frac{1}{\Gamma(1-\alpha_1)\Gamma(1-\alpha_2)}\left\{\ln\left(\frac{\alpha_1}{\alpha_2}\right) + \psi(1-\alpha_2) - \psi(1-\alpha_1) + \frac{1}{2\alpha_2} - \frac{1}{2\alpha_1}\right\} = 0. \tag{52}$$

Then α must be the natural number and the energy levels for s states are

$$E_n = -\frac{\hbar^2}{2ma_0^2 n^2} \quad (n = 1,2,3, \ldots) \tag{53}$$

It is worth noting that before the energy quantization by the orthogonality criterion, the Whittaker function (22) is not divergent and turns to zero at the origin. The functions are quadratic integrable and the α are continuous. The usual standard conditions cannot quantize the energy. It is the orthogonality criterion, rejecting all the continuous bound states and selecting all the s states, which are experimentally observable.

Unlike the 1D case, all the s states in 3D have even parity. The continuity of the wave functions is not a problem. The derivative connection can be proved as

$$\frac{\partial \psi}{\partial r} = -\frac{1}{a_0\sqrt{4\pi}} \lim_{r_0 \to 0} \int_0^{r_0} u(r)dr = 0. \tag{54}$$

It can be proved that when $\alpha = n$, this condition is definitely satisfied.

It is very interesting to study the existence problem of the state $u_0 = Ce^{-\xi/2}$. In Loudon's theory, this state will be accepted. But Andrews thought that this state would not be observable due to the vanishing scalar products with other states. But in our theory, only in the generalized quantum mechanics framework, including singular states, the orthogonality criterion can definitely reject this kind of singular state.

The examples in this section can provide a reliable basis for testing the correctness of the two theories, because the 3D H atom is the special example and in the experiment the 3D H atom is very clear. In the experiments, these states have not been observed. This means that the orthogonality criterion has stood the fact test.

For $\Gamma < \frac{1}{4}$ in Eq. (49), the orthogonality criterion can reject the states with higher-order singularity and accept those with lower-order singularity among these two kinds of singular states.

VIII. CONCLUDING REMARKS AND DISCUSSION

In order to fit the study of the singular state problem, it is necessary to generalize the quantum mechanics framework to include the singular states [21,22,25]. In this framework, due to the reality of the measured probability of dynamical quantities, the orthogonality criterion of the eigenfunctions is the same as the physical natural requirements [22]. These orthogonalities are usually satisfied automatically for regular states [22], but for singular states, the situations are different: sometimes they are very important and can reject many nonphysical states. Sometimes the energy levels are essentially determined by these orthogonality criteria. The energy levels of the 1D and the s states of the 3D hydrogen atoms discussed here are the exact soluble examples of the orthogonality criteria and consistent with the experiments. Moreover, these criteria are necessary to determine the energy quantization and reject the unphysical states.

For the 1D hydrogen atom problem there is a long history. This is also related to the study of the Wigner crystal [13,14] and the 1D exciton [7–12]. Loudon [2] pointed out the problems in the usual solutions. Then he expressed the general solutions by two linear-independent Whittaker functions. This is important progress. But a series of interesting problems are still waiting to be solved, which are closely related to the fundamental theory of singular states in quantum mechanics. (1) the energy quantization; (2) the Loudon even states and the nondegeneracy theorem breaking. In Loudon's paper [2], besides the odd states there exist degenerate even states simultaneously. They are considered as counterexamples of the nondegeneracy theorem [2,4]. In our paper, from a physical point of view, boundary conditions are the manifestation of the field equation. The natural connection condition for the wave function and its derivatives can be derived from the Schrödinger equation. These connection conditions showed that Loudon's even states do not satisfy this physical requirement and must be rejected definitely. So there are no such even states serving as counterexamples for the nondegeneracy theorem. (3) The question of the Loudon ground state and Andrews' question.

In Ref. [2], $\psi_0(\xi) = Ce^{-\xi/2}$ is suggested as the ground state, with infinite binding energy. With the aid of Schwarz's inequality, Andrews proved that the scalar products of ψ_0 with any quadratic integrable functions vanish. And he predicted that ψ_0 is not observable.

In this paper, we reconfirm that the ψ_0 state has a vanishing scalar product with all other finite wave functions. But we doubt the validity of Andrews' question: (a) The proof in Andrews' paper does not mean that ψ_0 is orthogonal with other states in the meaning of quantum mechanics. (b) If ψ_0 does exist, considering Andrews' argument, the energy of ψ_0 is $-\infty$. The 1D hydrogen atom will stay in the ψ_0 state. And the other states will not be excited. The unobservable state is not ψ_0, but other states. In experiments, other states have surely been observed. This means that the quantum mechanics need to provide a definite reason to reject this Loudon "ground state." This definite reason is the orthogonality criterion for singular states.

For the s state of the 3D hydrogen atom, there is almost the same problem. The orthogonality criterion can definitely reject Loudon's "ground state" with infinite binding energy. The highly accurate experimental data of the hydrogen atom are the touchstone for the orthogonality. Since it is proved that reason for rejecting ψ_0 state is the orthogonality criterion.

(4) Up to now, all the applications of the orthogonality

criteria have been successful, including a variety of singular states (with pole, essential singularity, or phase angle uncertainty). Now we add a kind of singular state (the derivative logarithmic singularity). We think that the generalized quantum mechanics framework, including singular states, in theory is reliable and trustworthy.

ACKNOWLEDGMENTS

One of the authors (D.X.) would like to express his sincere thanks to the financial support in part by the Chinese National Science Foundation and the Chinese High Education foundation, the Shanghai Foundation of Natural Science, the CEEC, NSF Grant No. DMR 91-22043, DARPA Grant No. MDA 972-88-G-002, the State of Texas, NASA Grant No. NAGW-977, Texas Center for Superconductivity at the University of Houston, and the T.L.L. Temple Foundation. He would also like to acknowledge Professor C. N. Yang, Professor W. E. Evenson, Professor P. H. Hor, Professor J. Qiu, Professor H. Chen, and Professor W. P. Su for their significant discussions and the ITP and the Department of Physics in SUNY at Stony Brook and TCS in UH for their hospitality. The authors would also like to thank Professor Patricia G. Patterson at the American Language Institute in New York University, Dr. Jeff Ramsay, and Dr. Austin Anthis for their great help in improving our English.

[1] S. Flugge and H. Marschall, *Rechenmethoden der Quantentheorie* (Springer-Verlag, Berlin, 1952), p. 69.
[2] R. Loudon, Am. J. Phys. **27**, 649 (1959).
[3] M. Andrews, Am. J. Phys. **34**, 1194 (1966).
[4] Zhao Shuchen, University Physics **5**, 23 (1986) (in Chinese).
[5] Dai Xianxi, Qiu Jilong, Hu Sizhu, Fudan J. **30** (3) (1991).
[6] V.L. Ginzburg, Contemp. Phys. **33**, 15 (1992).
[7] R.L. Elliott and R. Loudon, J. Phys. Chem. **8**, 382 (1959).
[8] R.L. Elliott and R. Loudon, J. Phys. Solids **15**, 196 (1960).
[9] A.J. Heeger, S. Kivelson, J.R. Schrieffer, and W.-P. Su, Rev. Mod. Phys. **60**, 781 (1988), and the references therein.
[10] Shuji Abe, J. Phys. Soc. Jpn. **58**, 62 (1989).
[11] Shuji Abe and W.P. Su, in Proceedings of Symposium on Photoinduced Charge Transfer, Rochester, June, 1990. [Mol. Cryst. Liq. Cryst. **194**, 357 (1991)].
[12] Shuji Abe (unpublished).
[13] E.P. Wigner, Trans. Faraday. Soc. **34**, 678 (1938).
[14] W.J. Carr, Jr., Phys. Rev. **122**, 1437 (1961).
[15] Dai Xianxi and Dai Jiqiong (unpublished).
[16] E.T. Whittaker and G.N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1927).
[17] A. Erdelyi, W. Magnus, F. Oberhettinger, and F. Tricomi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1953) Vol. 1.
[18] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics, Non-Relativistic Theory* (Pergamon Press, New York, 1958) (translated from Russian).
[19] Hu Sizhu, Dai Xianxi. Fudan J. (Natural Science) **30** (2) (1991).
[20] C.N. Yang, Phys. Rev. Lett. **19**, 1312 (1967).
[21] K.M. Case, Phys. Rev. **80**, 797 (1950).
[22] Dai Xianxi and Ni Guangjiong, Fudan J. (Natural Science) **16** (3), 1 (1977).
[23] Dai Xianxi, Fudan J, (Natural Science) **16**(1), 100 (1977).
[24] Dai Xianxi and Ni Guangjiong, Physica Energiae Fortis et Physica Nuclearies, **2** (3), 225 (1978).
[25] Dai Xianxi, Huang Fayan, and Ni Guangjiong, *Proceedings of the 1980 Guangzhou Conference on Theoretical Physics* (Science Press, Beijing, China, 1980), Vol. 2, pp. 1373–1389.
[26] Tai Tsun Wu and Chen Ning Yang, Nucl. Phys. **B107**, 365 (1976).
[27] Y. Kazama, Chen Ning Yang, and A.S. Goldhaber, Phys. Rev. D **15**, 2287 (1977).
[28] Wang Zhuxi and Guo Dungren, *An Introduction to the Special Functions* (Science Press, Beijing, 1979) (in Chinese).