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Breakdown of Bohr's Correspondence Principle

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Bohr's correspondence principle, i.e., the expectation that the semiclassical approximation works better for states with greater quantum numbers, is shown to break down in all quantum systems in which the asymptotic interaction between the fragments behaves as $-C_n/r^n$ with $n > 2$.

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From the early days of quantum mechanics, it has long been expected that the greater the quantum number for a certain degree of freedom (corresponding to a greater number of nodes in the corresponding wave function), the better the semiclassical approximation [1]. This expectation, which is often referred to as Bohr's correspondence principle, has persisted despite a lack of rigorous proof for an arbitrary potential. It works well in Coulombic systems and has been assumed to be a general principle partly because for systems in which the asymptotic interaction is of the form of $1/r^n$ with $n > 2$, the only *systematic* understanding of the highly excited bound spectra has been based on a semiclassical consideration [2] and there has been no corresponding quantum theory to compare with [3].

Stimulated by advances in cold-atom collisions, especially the development of photoassociative spectroscopy (see, e.g., [4–14]), considerable progress has been made in the understanding of the excited spectra of systems in which the asymptotic interaction is not Coulombic [4–21]. In particular, analytic solutions of the Schrödinger equation for $1/r^6$ and $1/r^3$ potentials have been obtained [18–21]. By comparing the fully quantum result based upon these solutions with the corresponding semiclassical prediction and also by examining the criterion for the applicability of the semiclassical approximation, we show the expectation that semiclassical results work better for more highly excited states is not applicable to systems in which the asymptotic potential is of the form of $-C_n/r^n$ with $n > 2$. In fact, we will show for such systems that the opposite is true, i.e., the semiclassical approximation

fails for the most highly excited states which are closest to the threshold, but can work better and better for lower-lying states which are less excited.

Consider a quantum system described by the radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{\hbar^2 l(l+1)}{2\mu r^2} + V(r) - \epsilon \right] u_l(r) = 0, \quad (1)$$

in which the potential $V(r)$ has an asymptotic behavior characterized by

$$V(r) \xrightarrow{r \rightarrow \infty} -C_n/r^n. \quad (2)$$

If the exponent n is greater than 2, there are only a finite number of bound states. Depending on the value of C_n and μ , this number can, however, be arbitrarily large. Specifically, if the length scale defined by

$$\beta_n \equiv (2\mu C_n/\hbar^2)^{1/(n-2)} \quad (3)$$

is much greater than other length scales present in the system, the corresponding quantum system has a large number of bound states. This condition can be conveniently summarized as

$$\beta_n \gg r_0, \quad (4)$$

where r_0 is roughly the longest of the other length scales in the system [22]. Since we are interested here only in the limit of a large quantum number and also for the purpose of comparing with the semiclassical results [2], the condition Eq. (4) will generally be assumed [23]. It is however worth noting that the limit specified by Eq. (4) is not only of purely theoretical interest. It is satisfied in

many real quantum systems as well, especially systems with an asymptotic $-C_3/r^3$ potential that is due to the resonant electric dipole-dipole interaction.

To be specific, consider first the case of $n = 3$ and $l = 0$. Under the condition of Eq. (4), the semiclassical result [2] for the highly excited states can be written as

$$[-\epsilon_s(v)]^{1/6} = \frac{[\Gamma(1/3)]^3}{2^{5/3}3^{1/2}\pi} (v_{\max} - v + \mu_D), \quad (5)$$

where ϵ_s is a scaled bound-state energy defined by

$$\epsilon_s = \frac{1}{4} \frac{\epsilon}{(\hbar^2/2\mu)(1/\beta_3)^2}. \quad (6)$$

v is a (vibration) quantum number, v_{\max} is the quantum number corresponding to the most highly excited bound state, and μ_D is a constant that depends on interactions having shorter range. This equation is similar in spirit to the Rydberg formula for Coulombic systems. It has been used, for example, to extract the C_3 coefficient from a photoassociative spectrum [5,7,13].

The key implication of this semiclassical result is that the spacing $[-\epsilon_s(v-1)]^{1/6} - [-\epsilon_s(v)]^{1/6}$ is a universal constant ($= 1.11291267\dots$) that is the same for *all* systems with an asymptotic $-C_3/r^3$ interaction [provided that the condition Eq. (4) is satisfied]. It is independent of both C_3 and μ , which scale only the energy, independent of the quantum number v , and is furthermore independent of the short-range part of the potential, which comes into play only through the constant μ_D . And according to the correspondence principle, one would expect this conclusion to work better and better for greater quantum numbers v [2], an assertion which we show to be incorrect.

Quantum mechanically, the bound spectrum of a system described by Eqs. (1) and (2) with $n = 3$ can be formulated rigorously as the crossing points between a universal function of the scaled energy ϵ_s [defined by Eq. (6)] and a function of energy which depends only on interactions having shorter range [21]. Specifically, it is given by the solutions of

$$\chi_l(\epsilon_s) = K_l^0(\epsilon). \quad (7)$$

Here K_l^0 is a short-range K matrix that is related to the logarithmic derivative of the wave function as in [20]. χ_l is a function of ϵ_s determined by the analytic solutions of the Schrödinger equation for an attractive $1/r^3$ interaction [21]. Specifically,

$$\chi_l(\epsilon_s) = \tan\pi(\nu - \nu_0) \frac{1 - M_{\epsilon l}}{1 + M_{\epsilon l}}, \quad (8)$$

in which ν and $M_{\epsilon l}$ are the same as those defined for the repulsive $1/r^3$ potential [20] [the derivation of Eqs. (7) and (8) and a complete discussion of the attractive $1/r^3$ solutions are presented elsewhere [21], but the methodology can already be found in [18–20]]. The function χ_l for a specific l is universal in the sense that it is the same for all quantum systems with $V(r) \rightarrow -C_3/r^3$. Different systems differ from each other only in the scaling of

energy, determined by C_3 and μ , and in $K_l^0(\epsilon)$, which is determined by interactions having shorter range. A plot of $\chi_{l=0}$ versus $-(-\epsilon_s)^{1/6}$ is shown in Fig. 1. The s wave bound spectrum of any potential with $V(r) \rightarrow -C_3/r^3$ at large distances is given by the crossing points of this function with a system specific $K_l^0(\epsilon)$. Also plotted, as an example, are the vibration energy levels for both the 0_g^- and the 1_u electronic states of $^{23}\text{Na}_2$ computed numerically by Stwalley *et al.* [15]. These two electronic states have different values of C_3 , but their vibration energy levels can be plotted on the same diagram with a proper scaling.

This quantum result is completely general and is applicable even when the condition Eq. (4) is violated. The only difference is that K_l^0 would then have more significant energy dependence. For our purposes here, we are interested only in the limit of large quantum numbers under the condition of Eq. (4). In this case, the quantum spectrum for the highly excited states simplifies to the crossing points of χ_l with $K_l^0 = \text{constant}$ [19]. This result, which is exact in the limit of $\beta_n/r_0 \rightarrow \infty$ (implying $v_{\max} \rightarrow \infty$), is simply due to the fact that, near the threshold, the dominant long-range interaction induces an energy dependence on the scale of $(\hbar^2/2\mu)(1/\beta_n)^2$, while the energy dependence induced by interactions having a shorter range occurs only over a much greater scale characterized by $(\hbar^2/2\mu)(1/r_0)^2$. The vibrational energy levels plotted in Fig. 1 for the 0_g^- and the 1_u electronic states of $^{23}\text{Na}_2$ [15] are good illustrations of this point. They show that $\chi_l(\epsilon_s)$ evaluated at the highly excited bound-state energies [= $K_l^0(\epsilon)$ at these energies]

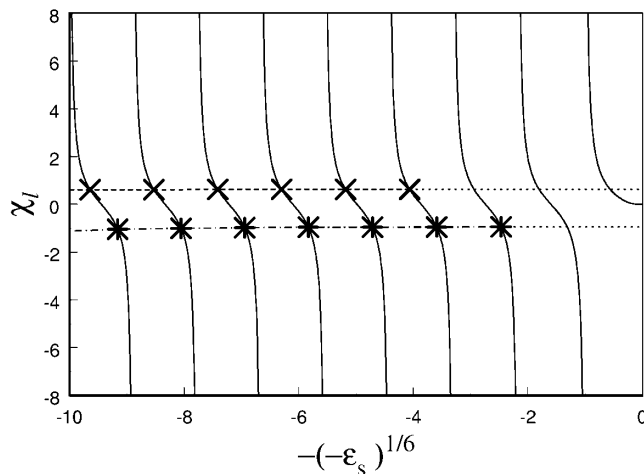


FIG. 1. Solid line: the χ_l function for an attractive $1/r^3$ interaction with $l = 0$, plotted vs $-(-\epsilon_s)^{1/6}$. The s wave bound spectrum of any potential with $V(r) \rightarrow -C_3/r^3$ at large distances is given by the crossing points of this function with a short-range parameter $K_l^0(\epsilon)$. For systems that satisfy $\beta_3 \gg r_0$, $K_l^0(\epsilon)$ is approximately a constant in the threshold region. The crosses and the stars represent the vibrational energy levels for the 0_g^- and the 1_u electronic states of $^{23}\text{Na}_2$, respectively. They are obtained from a quantum numerical calculation in [15]. The dotted lines represent constant extrapolations of $K_{l=0}^0$, from which the energies of the higher bound states can be obtained.

have indeed very little energy dependence. This is in spite of the fact that the 1_u electronic state supports only 14 vibrational levels, which is not a “large” number.

Table I lists the quantum results of the spacing $[-\epsilon_s \times (\nu - 1)]^{1/6} - [-\epsilon_s(\nu)]^{1/6}$ calculated from the crossing points of $\chi_{l=0}$ with three constant values of $K_{l=0}^0$. It shows clearly the breakdown of the semiclassical approximation close to the threshold. Specifically, the spacing depends on the quantum number ν . It is also different for different values of $K_{l=0}^0$, implying a dependence on interactions having shorter range. It is also clear from this comparison that the semiclassical approximation does get better for the less excited states away from the threshold where the dependences of the spacing on both the quantum number ν and on the parameter $K_{l=0}^0$ become less and less significant.

The differences between the quantum and the semiclassical predictions of the spacing $[-\epsilon_s(\nu - 1)]^{1/6} - [-\epsilon_s(\nu)]^{1/6}$ translate, of course, into different predictions for binding energies. In the example of the 0_g^- state of $^{23}\text{Na}_2$, the last three bound-state energies were not computed quantum mechanically [15]. They were obtained from an extrapolation based on the semiclassical approximation [2]. Table II compares the results of this extrapolation with that of a quantum extrapolation (see Fig. 1), and significant differences can be seen especially for the least bound state [24]. This difference becomes even more obvious for the 1_u electronic state [15]. The semiclassical extrapolation predicts in this case two more bound

TABLE I. Quantum results for $[-\epsilon_s(\nu - 1)]^{1/6} - [-\epsilon_s(\nu)]^{1/6}$ for the s wave bound spectra of systems with $n = 3$ and $\beta_3 \gg r_0$. Smaller values of $\nu_{\max} - \nu$ correspond to more highly excited states.

$\nu_{\max} - \nu$	$K_{l=0}^0 = 0.2$	$K_{l=0}^0 = 0.5$	$K_{l=0}^0 = 2.0$
0	1.319051	1.255099	1.193940
1	1.140453	1.138031	1.133384
2	1.124471	1.123821	1.122464
3	1.119314	1.119046	1.118466
4	1.116986	1.116851	1.116549
5	1.115735	1.115657	1.115480
6	1.114985	1.114935	1.114823
7	1.114499	1.114466	1.114390
8	1.114166	1.114143	1.114089
9	1.113928	1.113911	1.113872
10	1.113752	1.113739	1.113709
11	1.113618	1.113608	1.113585
12	1.113514	1.113506	1.113488
13	1.113431	1.113425	1.113410
14	1.113364	1.113359	1.113348
15	1.113310	1.113306	1.113296
16	1.113265	1.113261	1.113253
17	1.113227	1.113224	1.113217
18	1.113194	1.113192	1.113186
	\vdots	\vdots	\vdots
Semiclassical	1.112913	1.112913	1.112913

states with binding energies of $3.8739 \times 10^{-8} \text{ cm}^{-1}$ and $1.2735 \times 10^{-12} \text{ cm}^{-1}$, respectively, while the quantum extrapolation (see Fig. 1) predicts only one more bound state with a binding energy of $3.2367 \times 10^{-8} \text{ cm}^{-1}$ [24].

The breakdown of the semiclassical approximation near the threshold for $n > 2$ is not entirely surprising. The fact that one had to use a combination of semiclassical and quantum theory to obtain the scattering length [25] was an indication that a pure semiclassical theory might fail for the most highly excited bound states. This failure is also consistent with the standard criterion for the applicability of the semiclassical approximation [25,26]

$$\left| \frac{d}{dr} \frac{1}{k(r)} \right| \ll 1, \quad (9)$$

where $k(r) = \{(2\mu/\hbar^2)[\epsilon - V(r)]\}^{1/2}$. For a $-C_n/r^n$ potential, the classical outer turning point at energy ϵ is at

$$r_t = (\kappa \beta_n)^{-2/n} \beta_n, \quad (10)$$

where κ is related to energy by $\epsilon = -(\hbar^2/2\mu)\kappa^2$. At the same time, Eq. (9) leads to the requirement

$$(r/\beta_n)^{(n-2)/2} \ll 1, \quad (11)$$

which translates into $r \ll \beta_n$ for $n > 2$. Comparison of this criterion with Eq. (10) indicates that as the energy approaches the threshold, there is an increasingly expanded part of the *classically allowed* region in which the semiclassical condition is violated. One can thus expect the breakdown of the semiclassical approximation near the threshold to be a general characteristic of *all* long-range interactions of the type of $-C_n/r^n$ with $n > 2$. In particular, the semiclassical quantization results of LeRoy and Bernstein [2] are expected to fail for the last few bound states with binding energies that are not much greater than $(\hbar^2/2\mu)(1/\beta_n)^2$.

This conclusion is also verified for potentials with an attractive $1/r^6$ asymptotic behavior [18,19]. Under the condition of Eq. (4), a semiclassical approximation for the highly excited s states leads to [2]

$$[-\epsilon_s(\nu)]^{1/3} = \frac{[\Gamma(1/3)]^3}{2^{5/3}\pi} (\nu_{\max} - \nu + \mu_D), \quad (12)$$

where ϵ_s is a scaled bound-state energy defined by

$$\epsilon_s = \frac{1}{16} \frac{\epsilon}{(\hbar^2/2\mu)(1/\beta_6)^2}. \quad (13)$$

TABLE II. Comparison of the binding energies $-\epsilon$ for the last three bound states of $^{23}\text{Na}_2$ in the 0_g^- state, predicted by a semiclassical extrapolation and by a quantum extrapolation, respectively.

ν	Semiclassical ^a (cm^{-1})	Quantum ^b (cm^{-1})
39	4.1916×10^{-11}	0.92524×10^{-11}
38	1.1215×10^{-8}	1.0065×10^{-8}
37	1.9247×10^{-7}	1.8908×10^{-7}

^aFrom [15]; ^bsee Fig. 1.

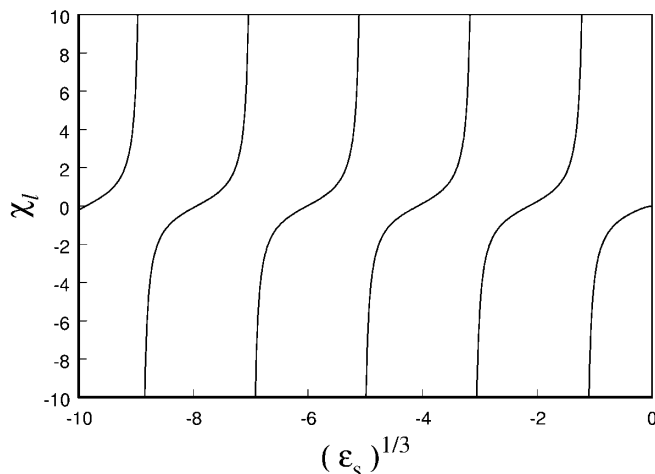


FIG. 2. The $\chi_l(\epsilon_s)$ function for the attractive $1/r^6$ interaction with $l = 0$ [18] plotted vs $(\epsilon_s)^{1/3}$. For systems satisfying $\beta_6 \gg r_0$, the highly excited s wave bound spectrum is given by the cross points of this function with a constant representing $K_{l=0}^0$.

Equation (12) asserts that the spacing $[-\epsilon_s(v-1)]^{1/3} - [-\epsilon_s(v)]^{1/3}$ is a universal constant ($= 1.92762\dots$) that is independent of C_6 and μ , independent of v , and independent of the short-range part of the potential. Quantum mechanically, the corresponding spectrum is given by the crossing points between a universal χ_l function derived from the attractive $1/r^6$ solutions [18,19] and a constant. Figure 2 shows this $\chi_{l=0}$ function plotted versus $(\epsilon_s)^{1/3}$. A comparison between quantum and semiclassical predictions of the spacing $[-\epsilon_s(v-1)]^{1/3} - [-\epsilon_s(v)]^{1/3}$ is presented in Table III. It again shows the breakdown of semiclassical predictions close to the threshold.

In conclusion, we have shown that Bohr's correspondence principle, which originated and worked well for Coulombic systems, does not apply to systems in which the asymptotic interaction is of the form of $-C_n/r^n$ with $n > 2$. In such systems, the semiclassical approximation fails near the threshold but can work better away from it until eventually interactions having shorter range come into play.

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TABLE III. Quantum results for $[-\epsilon_s(v-1)]^{1/3} - [-\epsilon_s(v)]^{1/3}$ for the s wave bound spectra of systems with $n = 6$ and $\beta_6 \gg r_0$. Smaller values of $v_{\max} - v$ correspond to more highly excited states.

$v_{\max} - v$	$K_l^0 = -0.2$	$K_l^0 = -0.5$	$K_l^0 = -2.0$
0	2.03581	1.99746	1.96296
1	1.93747	1.93648	1.93464
2	1.93131	1.93108	1.93061
3	1.92955	1.92947	1.92928
	\vdots	\vdots	\vdots
Semiclassical	1.92762	1.92762	1.92762

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