

## Lecture 6: Quantum-Classical Correspondence

### I. Bohr's Correspondence Principle

Turning back to Bohr atomic description it provides the frequency of emitted waves (photons) when the transition between two states in an atom takes place:

$$\begin{aligned} \nu_{n_1 \rightarrow n_2} &= \frac{E_2 - E_1}{h} = \frac{m_0 e_0^4}{8\epsilon_0^2 \hbar^3} Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R_\infty c Z^2 \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ &= R_\infty c Z^2 \frac{(n_2 - n_1)(n_2 + n_1)}{n_1^2 n_2^2}, \quad n_2 > n_1 \end{aligned}$$

Now, the main question is when this transition frequency is becoming eventually equal with the frequencies associated with the orbital circular motion on states "1" and "2", individually. For responding in this one may notice that the Bohr quantification supports the classical counterpart picture of electronic circular movement at optimum distance around the nucleus, with the angular velocity  $\dot{\phi}$  and the revolution frequency  $f$ , linked by the equation:

$$T_{opt,n} = \frac{m_0 v_{opt,n}^2}{2} = \frac{1}{2} m_0 (r_{opt,n} \dot{\phi})^2 = \frac{1}{2} m_0 r_{opt,n}^2 (2\pi f_n)^2$$

from where we have:

$$f_n = \frac{1}{2\pi \hbar n} \frac{e_0^4 m_0}{(4\pi\epsilon_0)^2 \hbar^2} \left( \frac{Z}{n} \right)^2 = \frac{2T_{opt,n}}{nh} = \frac{2R_\infty c Z^2}{n^3}$$

Now, the relation between the quantum transition frequency  $\nu_{n_1 n_2}$  and the "classical" ones associated to the quantum states  $n_1$  and  $n_2$ ,  $f_{n_1}$  and  $f_{n_2}$ , can be clarified in two limiting cases.

- When is about first neighbor high levels, i.e.  $\Delta n = n_2 - n_1 = 1$  &  $n_1, n_2 \gg 1$ , we have in asymptotical sense that  $n_1 \cong n_2$  leading with classical-quantum equivalency

$$\nu_{n_1 \cong n_2} = \frac{2R_\infty c Z^2}{n_1^3} = f_{n_1} = \frac{2R_\infty c Z^2}{n_2^3} = f_{n_2}$$

- When is about non-first neighbor but still high levels, i.e.  $\Delta n = n_2 - n_1 > 1$  &  $n_1, n_2 \gg 1$ , so that  $n_1 \cong n_2 \gg \Delta n$  we get the classical-quantum connection as:

$$\nu_{n_1 \cong n_2} = \frac{2R_\infty c Z^2}{n_1^3} \Delta n = \frac{2R_\infty c Z^2}{n_2^3} \Delta n = f_{n_1 \cong n_2} \Delta n$$

Therefore, the rule is that as much the quantum levels are higher as the quantum and classical frequencies approaches each other, establishing the so called Bohr correspondence principle between the quantum and classical “worlds”.

An even more striking and practical form of Bohr correspondence principle may be unfold since we introduce the counter of the quantum transition states as:

$$\Delta I = h\Delta n$$

that combined with Bohr quantum transition principle

$$\Delta E = h\nu_{\Delta n}$$

provides the quantum frequency under the form

$$\nu_{\Delta n} = \frac{\Delta E}{\Delta I} \Delta n$$

to be compared with the classical frequency of the state with  $E_n$ , recognized to can be written as

$$f_n = \frac{1}{h} \frac{dE_n}{dn} = \frac{dE_n}{dI} = \frac{\nu_{\Delta n}}{\Delta n}$$

Leading with the idea tha both frequencies approach each other when the slopes of the secant of spectrum lines equals the slopes of the tangents on the initial and final points on the graph

$$E_n = E_n(I_{n,\varphi}),$$

being here  $I_{n,\varphi}$  recognized as the phase integral

$$I_{n,\varphi} = \oint p_\varphi d\varphi = nh$$

since providing the angular momentum quantification,

$$p_\varphi = n\hbar = m_0 r_{opt,n}^2 \dot{\varphi},$$

in accord with above kinetic energy quantification – where the classical frequency was rooted. Note that the accompanying radial integral

$$I_{n,r} = \oint p_r dr = nh$$

gives nothing less than the starting de Broglie-Heisenberg-Bohr quantification. Also note that while Bohr model considers angular and radial integrals being quantified by the same quantum number  $n$ , further discrimination between them opens the way to treat 2D-elliptic Sommerfeld orbital description. However, while

the last approach is still not the general one we prefer to directly treat the 3D-case, however in detail in the next volume of the series.

**Table 1.I.** Check of the correspondence principle for asymptotic Bohr's hydrogen atom levels<sup>1</sup>.

Quantum states		Orbit frequency [s <sup>-1</sup> ]		Transition
Initial	Final	Initial	Final	Frequency [s <sup>-1</sup> ]
2	1	0.82 · 10 <sup>15</sup>	2.47 · 10 <sup>15</sup>	6.58 · 10 <sup>15</sup>
6	5	3.04 · 10 <sup>13</sup>	4.02 · 10 <sup>13</sup>	5.26 · 10 <sup>13</sup>
10	9	6.58 · 10 <sup>12</sup>	7.71 · 10 <sup>12</sup>	9.02 · 10 <sup>12</sup>
25	24	4.21 · 10 <sup>11</sup>	4.48 · 10 <sup>11</sup>	4.76 · 10 <sup>11</sup>
101	100	6.383 · 10 <sup>9</sup>	6.479 · 10 <sup>9</sup>	6.576 · 10 <sup>9</sup>
501	500	5.229 · 10 <sup>7</sup>	5.245 · 10 <sup>7</sup>	5.261 · 10 <sup>7</sup>

The **Table 1.I** further illustrates the Bohr quantum-classical correspondence principle.

## II. Moseley Law and Spectral Atomic Periodicity

Atomic Bohr's spectra are based from the transition energies given before; however, we may identify the so called spectral term

$$T_n = \frac{R_\infty Z^2}{n^2}$$

allowing to rewrite the spectral transition in terms of the wave-number (the so called *Rayleigh-Ritz principle*):

$$\tilde{\nu}_{n_1 n_2} = \frac{1}{\lambda_{n_1 n_2}} = \frac{\Delta E_{n_1 n_2}}{hc} = T_{n_1} - T_{n_2}$$

Still, for a many-electronic atom, the hydrogenic Bohr treatment can be still preserved with the price of introducing the so called shielding constant  $\sigma$

$$T_n^* = \frac{R_\infty (Z - \sigma)^2}{n^2}$$

that eventually depends on the shell's quantum number  $n$  (and of its further sub-shell's refinement). The last relationship may be further transformed to get the linear  $Z$ -dependency:

<sup>1</sup> See H. E. White, *Introduction to Atomic Spectra*, McGraw-Hill, Inc., New York, 1934, pp. 40

$$\sqrt{\frac{T_n^*}{R_\infty}} = \frac{1}{n}(Z - \sigma)$$

telling that the spectral terms for a given shell are proportional with the inverse of the quantum number of that shell. This has fundamental phenomenological interpretation for periods and groups of periodic Table: paractically, for the the different periods down groups it displays the increasing  $n$  so the diminishing angle of the fitted lines among the K, L, M, etc. transitions; whereas within periods, as the  $Z$  increases the squared of the spectral term to the Rydberg constant contribution increases.

Yet, for practical use the frequency is to be employed, rather than individual spectral terms; in this case one firstly has in generally that:

$$\nu_{n_1 n_2} = \frac{c}{\lambda_{n_1 n_2}} = c(T_{n_1} - T_{n_2}) = cR_\infty \left[ \frac{(Z - \sigma_1)^2}{n_1^2} - \frac{(Z - \sigma_2)^2}{n_2^2} \right]$$

while if assuming the same initial and final shielding constant,  $\sigma_1 \cong \sigma_2 = \sigma$ , the simplified squared root transition frequency is obtained as the generalized Moseley law:

$$\sqrt{\nu_{n_1 n_2}} = (Z - \sigma) \sqrt{cR_\infty \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]}.$$

As a specialization, for instance, for K lines ( $n_1=1, n_2=2$ ) the shielding constants can be further assumed as  $\sigma \cong 1$  so that the Moseley working formula is obtained:

$$\sqrt{\nu_{K\alpha}} = \frac{(Z-1)}{2} \sqrt{3cR_\infty} \cong (Z-1) \sqrt{2.48 \times 10^{15} \text{ (Hz)}}$$

Note that the Moseley rule is less exact comparing with the spectral terms' interpretation of periodic spectra of elements through assuming the same shielding constants between the paired levels considered. Still, for  $K\alpha$  lines it behaves in fair agreement with experiment see [Table 1.II](#) though comparing with theoretical yield:

$$h\nu_{K\alpha} \cong 13.6[\text{eV}] \frac{3}{4} (Z-1)^2 = 10.2(Z-1)^2 [\text{eV}].$$

Finally, note that the difference between the spectral term and frequency pictures of the Moseley law is the same as that between the orbital motion frequencies and the transition frequencies between two (Bohr) levels.

Moreover, the Moseley law may be regarded also as provided the atomic number  $Z$  in terms of structural quantum information including spectral terms, energies, shielding constants; in other words, atomic  $Z$  may be seen as a measure of such inner quantum structure merely as the given constant for an atom.

**Table 1.II** Experimental  $K\alpha_2$  (or  $KL_2$ : transition from the level  $L_2$  with  $n=2$ ,  $l=1$  and  $j=1/2$  to the level  $K$  with  $n=1$  and  $l=0$ ) X-ray energies, in eV, with experimental uncertainty in parenthesis, as compared with computed ones from the Moseley law, for the third and fourth periodic groups of elements. <sup>2</sup>

<i>Z</i>	<i>Element</i>	<i>K<math>\alpha_2</math> [eV]</i>	
		<i>Experimental(unc.)</i>	<i>Computed</i>
11	Na	1040.98(12)	1020
12	Mg	1253.437(13)	1234.2
13	Al	1486.295(10)	1468.8
14	Si	1739.394(34)	1723.8
15	P	2012.70(48) *	1999.2
16	S	2306.700(38)	2295
17	Cl	2620.846(39)	2611.2
18	Ar	2955.566(16)	2947.8
19	K	3311.1956(60)	3304.8
20	Ca	3688.128(49)	3682.2
21	Sc	4085.9526(85)	4080.
22	Ti	4504.9201(94)	4498.2
23	V	4944.671(59)	4936.8
24	Cr	5405.5384(71)	5395.8
25	Mn	5887.6859(84)	5875.2
26	Fe	6391.0264(99)	6375.
27	Co	6915.5380(39)	6895.2
28	Ni	7461.0343(45)	7435.8
29	Cu	8027.8416(26)	7996.8
30	Zn	8615.823(73)	8578.2
31	Ga	9224.835(27)	9180.
32	Ge	9855.42(10)	9802.2
33	As	10507.50(15)	10444.8
34	Se	11181.53(31)	11107.8
35	Br	11877.75(34)	11791.2
36	Kr	12595.424(56)	12495.

\* Interpolated from nearby elements.

<sup>2</sup> Experimental data from <http://physics.nist.gov/PhysRefData>