Lecture Thursday 27. September 2007

Topics: In lecture: Density Functional Theory Here: Spectroscopy

Comments

Version Tuesday 02. 10. 2007 morning (Final)

Material in Lecture: Kohn' Nobel Lecture; A PDF of talk on DFT (notes will be added)

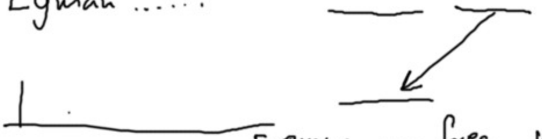
"Blackboard" - Spectroscopy – and Spectra Terms

Final Question: Why are the TERMS energetically different

Spectroscopy of Hydrogen

Balmer, Rydberg, Paschen-Back.....

Lyman ......



Energies ... freq ... wavelengths

Helium → more fun ; singly excited

still mostly easy ....

1s2p 1s3p ← (others autoionizing)

1s2s

TERMS $\boxed{2p\,3p}$

TERMS → $\underline{\text{ENERGY}}$

$|n_1 l_1 m_1\rangle \quad |n_2 l_2 m_2\rangle$

$R_{n_1}(r_1)\, Y_{l_1 m_1}(\hat{r}_1) \quad R_{n_2}(r_2)\, Y_{l_2 m_2}(\hat{r}_2)$

$\vec{l}_1, \vec{l}_2 \quad \ldots\, \vec{l}_1^{\,2} \ldots\, l_1(l_1+1) \ldots$

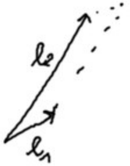
$(\vec{l}_1 + \vec{l}_2) \to \vec{L} \quad \vec{L}^2 \ldots \quad L(L+1)$

$\vec{S}$ 0 1 2

$L \le l_1 + l_2$

$L \ge |l_1 - l_2|$

Triangle rule for l



$|l_1 - l_2| \le L \le l_1 + l_2$

$\boxed{(2p\,3p)\,{}^{1}P_{J}}$ with ${}^{2S+1}$ and ${}_{J}$ — Spectr. notation

$\vec{J} = \vec{L} + \vec{S}$ 0 1 2

How do we know the Ion. energies?
radiaton / monochromator (prism ?) Grating (Gitter)
Strong Source Photoelectrons -> Photoelectron spectroscopy

Excited states : Energy emitted - carried as light or El-Mag radiation - only special energies (discrete values) - discrete sets of frequencies (or) wavelengths; Line spectra

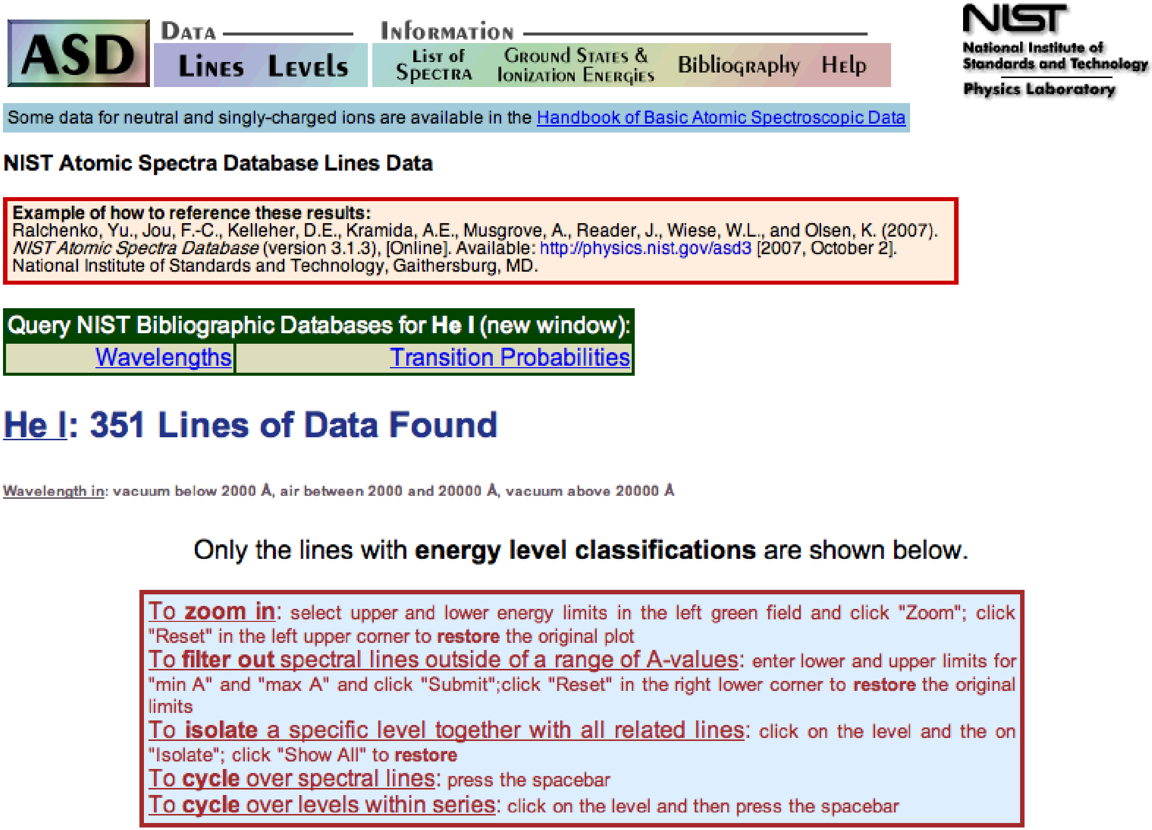
SPECTROSCOPY .... for analysis (or proof of presence) ... characteristic lines

spectra continuous -> solid state effects (condensed matter properties) Red glowing hot metal, white metal in a smith's workshop

Spectroscopic terminology (TERMS)
l_1 l_2 -> L selection rules
each of the L makes a "TERM" example 2p 3p L 0, 1, 2
2p 3p S 2p 3p P 2p 3p D singlet and triplet J- values

Why are the energies different ? The interaction integrals (mentioned in Helium)
Hydrogen – like Helium like - and more complex .... L-S coupling j-j coupling
Config. mixing (NEXT) GTO STO (slaters type orbitals, gaussian type orbitals)

This is the start of java Grotrian at (He I)
http://physics.nist.gov/PhysRefData/ASD/lines_form.html



Some data for neutral and singly-charged ions are available in the Handbook of Basic Atomic Spectroscopic Data

NIST Atomic Spectra Database Lines Data

Example of how to reference these results:
Ralchenko, Yu., Jou, F.-C., Kelleher, D.E., Kramida, A.E., Musgrove, A., Reader, J., Wiese, W.L., and Olsen, K. (2007). *NIST Atomic Spectra Database* (version 3.1.3), [Online]. Available: http://physics.nist.gov/asd3 [2007, October 2]. National Institute of Standards and Technology, Gaithersburg, MD.

Query NIST Bibliographic Databases for He I (new window):

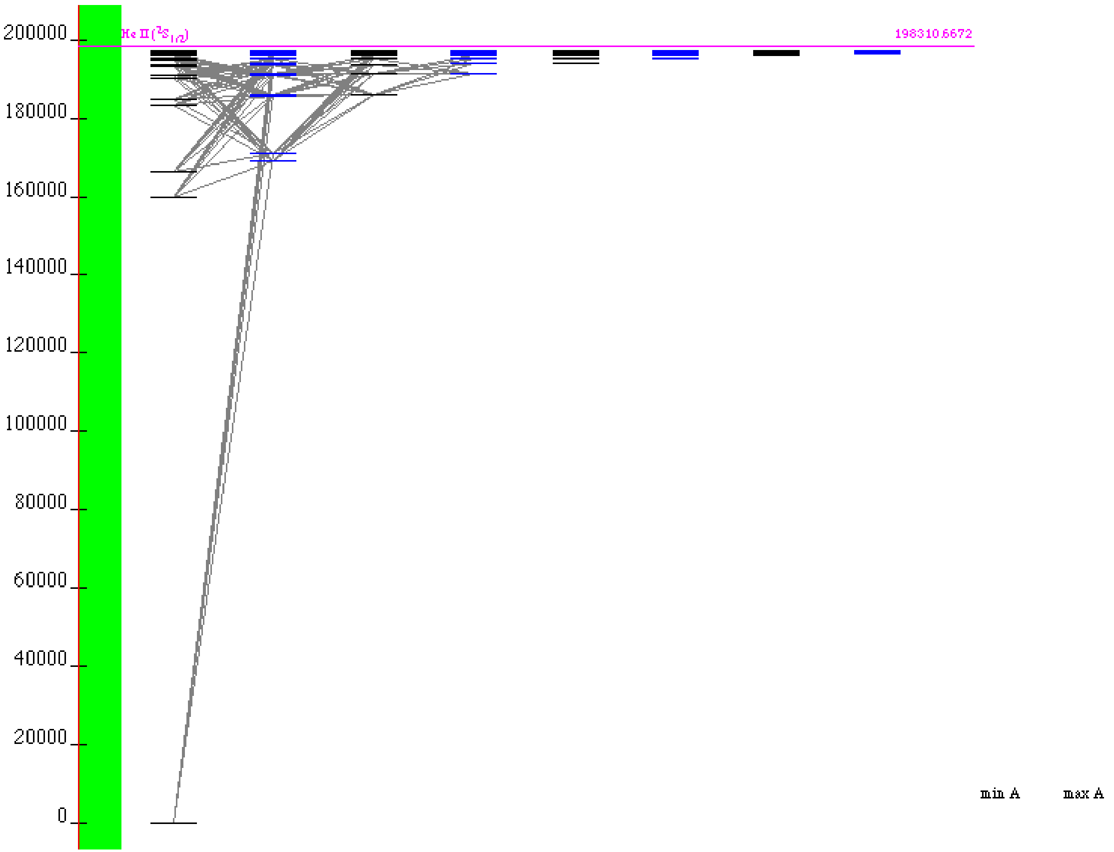
Wavelengths	Transition Probabilities

He I: 351 Lines of Data Found

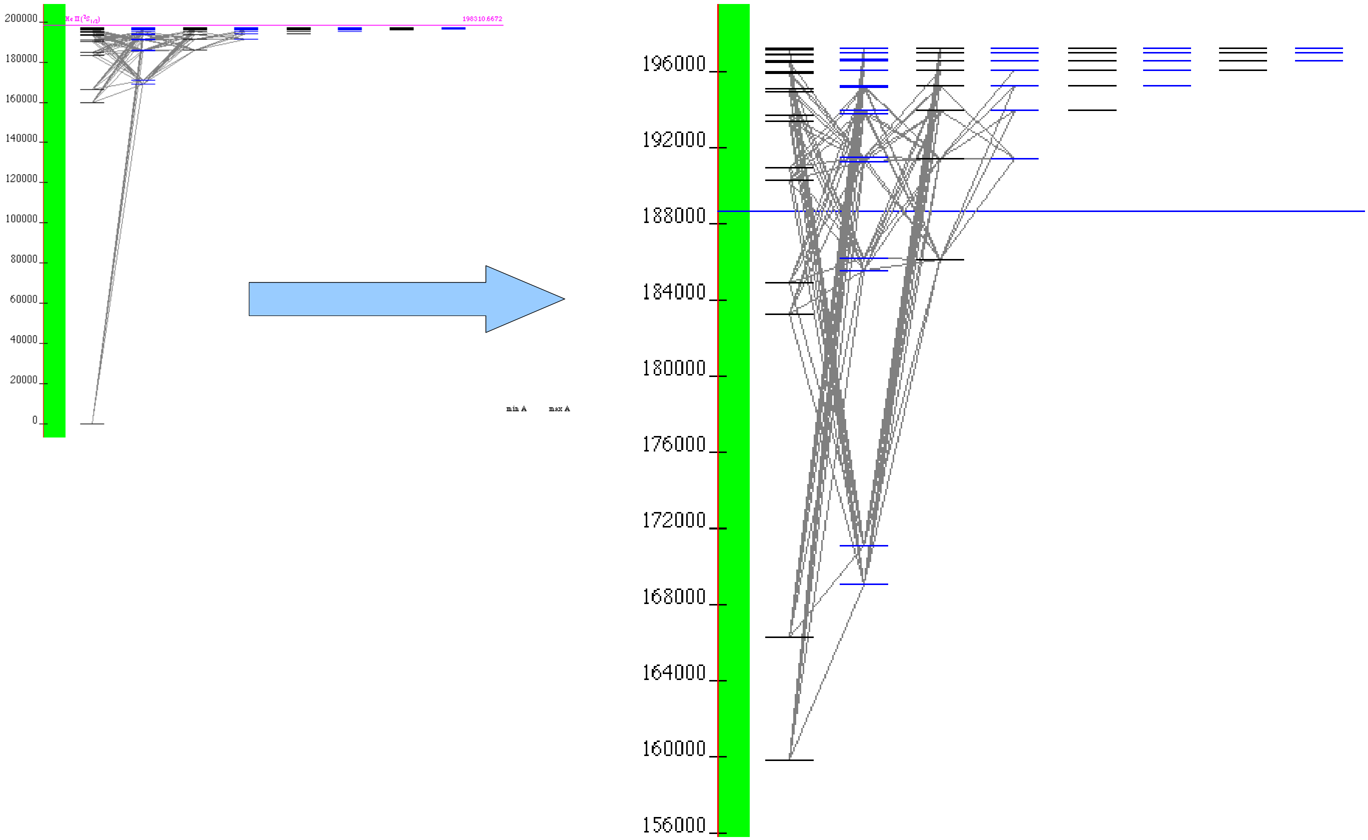
Wavelength in: vacuum below 2000 Å, air between 2000 and 20000 Å, vacuum above 20000 Å

Only the lines with **energy level classifications** are shown below.

To **zoom** in: select upper and lower energy limits in the left green field and click "Zoom"; click "Reset" in the left upper corner to **restore** the original plot
To **filter out** spectral lines outside of a range of A-values: enter lower and upper limits for "min A" and "max A" and click "Submit";click "Reset" in the right lower corner to **restore** the original limits
To **isolate** a specific level together with all related lines: click on the level and the on "Isolate"; click "Show All" to **restore**
To **cycle** over spectral lines: press the spacebar
To **cycle** over levels within series: click on the level and then press the spacebar



This is the java applet; You can zoom etc.   He I (neutral) He II (ionized once)
There is no He III - why? Is there Li III or Li IV, Carbon V ?



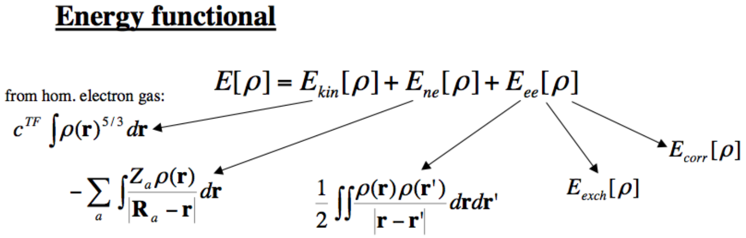
Zooming the upper part of spectrum

The DFT - Density Functional Theory has been discussed on the background of two PDF files: The Nobel Prize Lecture from Review of Modern Physics and a talk from Quantum chemistry (remember – many nuclei in molecules, not just one as in atoms)

Thomas-Fermi model as a sort of basis (electron density)
but built on orbitals; LDA local density approximation
orbitals – selfconsistent field method; Exchange and correlation added by a term.
Prof. Kohn: ... I begin with a provocative statement. In general the many-electron wave function $\Psi(r_1, \ldots, r_N)$ for a system of N electrons is not a legitimate scientific concept, when $N > N_0$, where N_0 is about 1000 .
The article gives a very nice introduction to Molecular Physics, Born-Oppenheimer, etc

More: Thomas Fermi Model and the exchange functional.
Is there a correlation term in full formulation?

From the talk:



Energy functional

$$E[\rho] = E_{kin}[\rho] + E_{ne}[\rho] + E_{ee}[\rho]$$

from hom. electron gas:

$$c^{TF} \int \rho(\mathbf{r})^{5/3} d\mathbf{r}$$

$$-\sum_a \int \frac{Z_a \rho(\mathbf{r})}{|\mathbf{R}_a - \mathbf{r}|} d\mathbf{r}$$

$$\frac{1}{2} \iint \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E_{exch}[\rho]$$

$$E_{corr}[\rho]$$