Atomic spectra of two-electron systems: He, Hg

Related topics

Parahelium, orthohelium, exchange energy, spin, angular momentum, spinorbit interaction, singlet series, triplet series, multiplicity, Rydberg series, selection rules, forbidden transitions, metastable state, energy level, excitation energy.

Principle and task

The spectral lines of He and Hg are examined by means of a diffraction grating. The wavelengths of the lines are determined from the geometrical arrangement and the diffraction grating constants.

Equipment

Spectrum tube, mercury	06664.00	1
Spectrum tube, helium	06668.00	1
Holders for spectral tubes, 1 pair	06674.00	1
Cover tube for spectral tubes	06675.00	1
Connecting cord, 50 KV, 1000 mm	07367.00	2
Object holder, 5×5 cm	08041.00	1
Diffraction grating, 600 lines/mm	08546.00	1
High voltage supply unit, 0-10 kV	13670.93	1
Insulating support	06020.00	2
Tripod base -PASS-	02002.55	1
Barrel base -PASS-	02006.55	1
Support rod -PASS-, square, l 400 mm	02026.55	1
Right angle clamp -PASS-	02040.55	3
Stand tube	02060.00	1
Meter scale, demo, l = 1000 mm	03001.00	1
Cursors, 1 pair	02201.00	1
Measuring tape, l = 2 m	09936.00	1

Problems

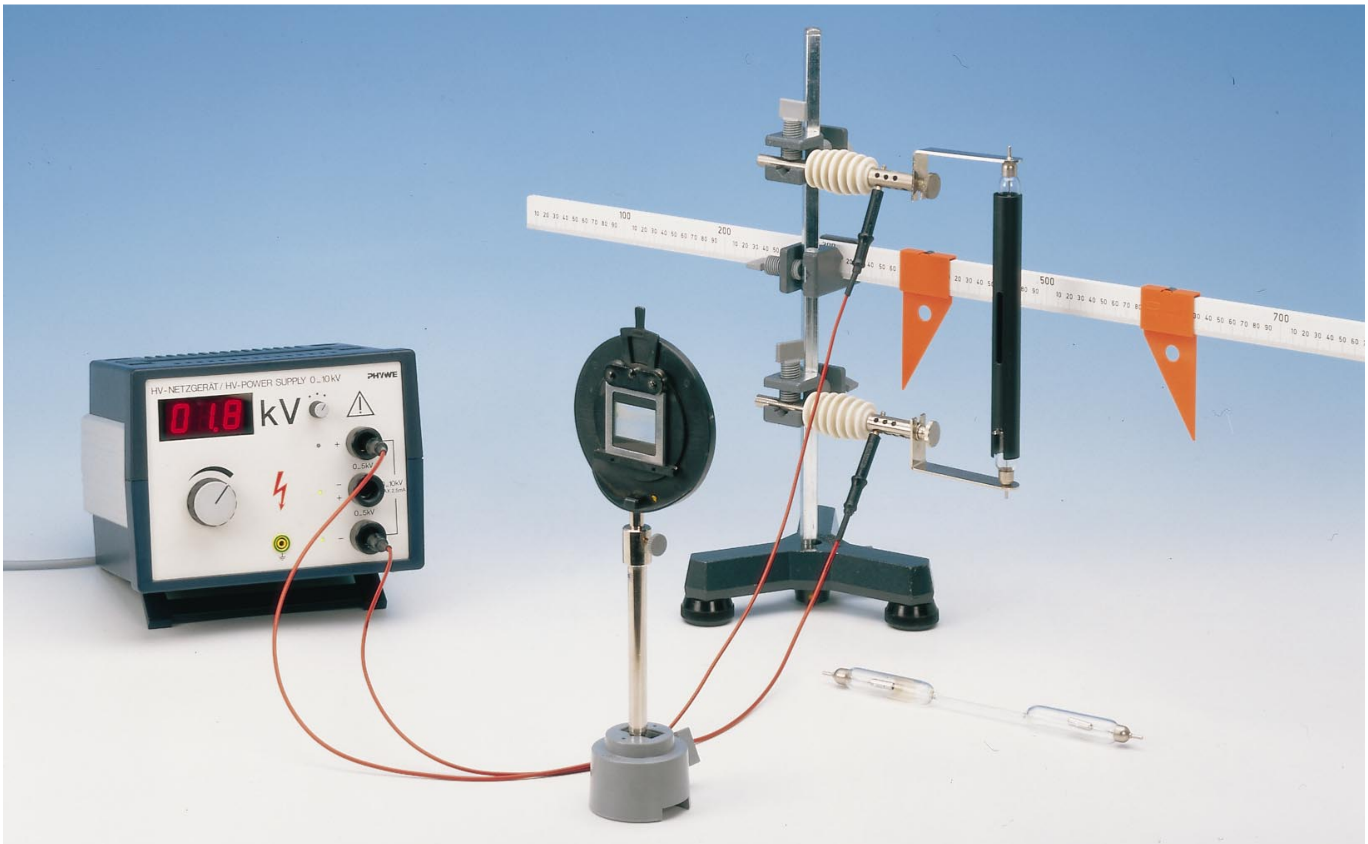
1. Determination of the wavelengths of the most intense spectral lines of He.
2. Determination of the wavelengths of the most intense spectral lines of Hg.

Set-up and procedure

The experimental set-up is shown in Fig. 1. Helium or mercury spectral tubes connected to the high voltage power supply unit are used as a source of radiation. The power supply is adjusted to about 5 kV. The scale is attached directly behind the spectral tube in order to minimize parallax errors. The diffraction grating should be set up at about 50 cm and at the same height as the spectral tube. The grating must be aligned so as to be parallel to the scale.
The luminous capillary tube is observed through the grating. The room is darkened to the point where it is still possible to read the scale. The distance 2 *l* between spectral lines of the same color in the right and left first order spectra are read without moving one's head. The distance d between the scale and the grating is also measured.

The individual lines (first order) of the spectral lamp are observed by means of the grating and the distance 2 *l* between equal lines is determined with the metre scale.

Fig.1: Experimental set up for measuring the spectra of He and Hg.



Theory and evaluation

1. If light of wavelength λ falls on a grating having a grating constant k, it is diffracted. Intensity maxima occur if the angle of diffraction which satisfies the condition:

$$n \cdot \lambda = k \cdot \sin \phi \; ; \; n = 0, 1, 2 \ldots$$

From Fig. 2. we have:

$$\sin \varphi = \frac{l}{\sqrt{d^2 + l^2}}$$

and hence

$$\lambda = \frac{k \cdot l}{\sqrt{d^2 + l^2}}$$

for the first-order diffraction.

2. Excitation of the He and Hg atoms results fromelectron impact. The energy difference produced when electrons revert from the excited state E_1 to the ground state E_0 is emitted as a photon with a frequency f.

$$hf = E_1 - E_0$$

where h = Planck's constant
= $6.63 \cdot 10^{-34}$ joule-seconds.

The Hamiltonian operator (non-relativistic) for the two electrons 1 and 2 of the He atom is:

$$H = -\frac{\hbar^2}{2m}\Delta_1 - \frac{\hbar^2}{2m}\Delta_2 - \frac{2e^2}{|\vec{r}_1|} - \frac{2e^2}{|\vec{r}_2|} + \frac{e^2}{|\vec{r} - \vec{r}_2|}$$

where $\hbar = \frac{h}{2\pi}$,

m and e represent the mass and charge of the electron respectively,

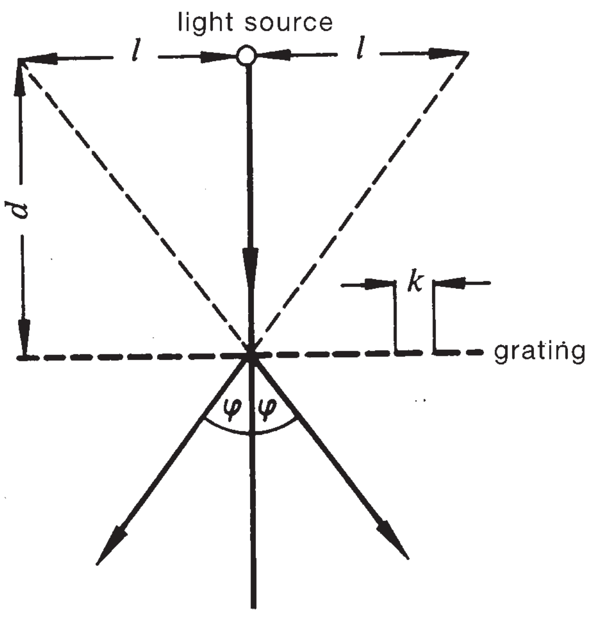


Fig. 2: Diffraction of light of wavelength λ at the grating.

$$\Delta_i = \frac{d^2}{dx_i^2} + \frac{d^2}{dy_i^2} + \frac{d^2}{dz_i^2}$$

is the Laplace operator, and $\vec{r}_i$ is the position of the i-th electron. The spin-orbit interaction energy

$$E_{so} \propto \frac{Z^4}{4 \cdot (137)^2}$$

was ignored in the case of the nuclear charge Z = 2 of helium, because it is small when Z is small.

If we consider $\frac{e}{|\vec{r}_1 - \vec{r}_2|}$ as the

electron-electron interaction term, then the eigenvalues of the Hamiltonian operator without interaction are those of the hydrogen atom:

$$E^0_{n,m} = -\frac{me^4}{8h^2}\left(\frac{1}{n^2} + \frac{1}{m^2}\right)$$

$$n, m = 1, 2, 3, \ldots .$$

As the transition probability for simultaneous two-electron excitation is very much less than that for one-elecron excitation, the energy spectrum of the system without interaction is:

$$E^0_{l,m} = -\frac{me^4}{8h^2}\left(1 + \frac{1}{m^2}\right)$$

$$m = 1, 2$$

The interaction term remores out the angular momentum degeneracy of the pure hydrogen spectrum and the exchange energy degeneracy. There results an energy adjustment:

$$E^1_{nl\pm} = \langle \phi^{\pm}_{nl\alpha} \left| \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \right| \phi^{\pm}_{nl\alpha} \rangle = C_{nl} \pm A_{nl}$$

in which $\phi^{\pm}_{nl\alpha}$ are the antisymmetricated non-interacted 2-particle wave functions with symmetrical (ϕ^+) or antisymmetrical (ϕ^-) position component, l^* is the angular momentum quantum number, and α is the set of the other quantum numbers required.

In the present case, the orbital angular momentum of the single electron l is equal to the total angular momentum of the two electrons L, since only one-particle excitations are being considered and the second electron remains in the ground state (l = 0).

C_{nl} and A_{nl} are the coulomb and exchange energy respectively. They are positive. Coupling the orbital angular momentum L with the total spin S produces for S = 0, i.e. ϕ^+, a singlet series and for S = 1, i.e. ϕ^-, a tirplet series. Because of the lack of spin-orbit interaction, splitting within a triplet is slight. As the disturbed wave functions are eigenfunctions for S^2 and as S^2 interchanges with the dipole operator, the selection rule

$$\Delta S = 0$$

(which is characteristic for 2-electron systems with a low nuclear-charge number) results and forbids transitions between the triplet and singlet levels.

In addition, independent of the spin-orbit interaction, the selection rule for the total angular momentum

$$\Delta J = 0, \pm 1$$

Fig. 3: Helium spectrum.

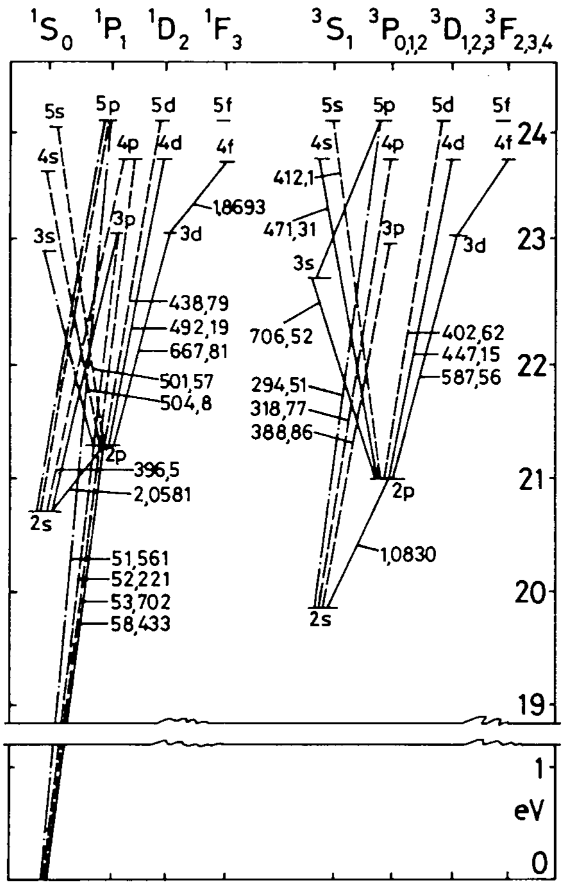
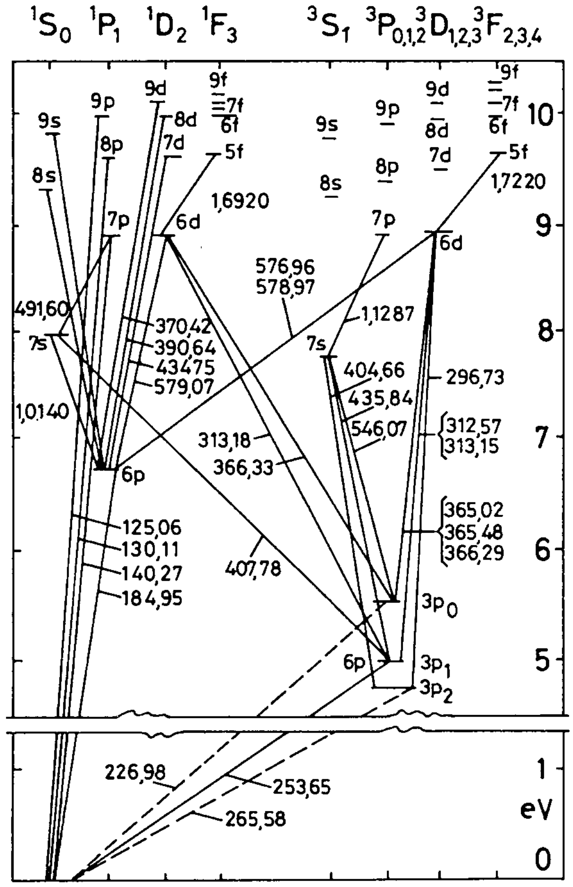


Fig. 4: Spectrum of mercury.



applies except where

$$J = 0 \rightarrow J' = 0 \, .$$

If the spin-orbit interaction is slight, then

$$\Delta L = 0, \pm 1$$

applies.

Detailed calculations produce the helium spectrum of Fig. 3.

The following table gives the measured lines:

Colour	λ/nm	Transition
red	665 ± 2	$3\,^1D \rightarrow 2\,^1P$
yellow-orange	586 ± 2	$3\,^3D \rightarrow 2\,^3P$
green	501 ± 2	$3\,^1D \rightarrow 2\,^1P$
blue-green	490 ± 2	$4\,^1D \rightarrow 2\,^1P$
blue	470 ± 3	$4\,^3S \rightarrow 2\,^3P$
violet	445 ± 1	$4\,^3D \rightarrow 2\,^3P$

Table 1: Measured spectral lines of He and the corresponding energy-level transitions.

The magnitudes of the exchange interaction and the Coulomb interaction of the two electrons can be estimated by comparing the energies of the transitions:

$$3\,^1D \rightarrow 2\,^1P$$
$$3\,^3D \rightarrow 2\,^3P$$

or

$$4\,^1D \rightarrow 2\,^1P$$
$$4\,^3D \rightarrow 2\,^3P$$

3. Hg, likewise, is a 2-electron system and possesses the structure of 2 series.

The spin-orbit interaction, however, is relatively pronounced so that only the total angular momentum

$$J = L + S$$

is a “good” conservation parameter. Splitting inside the triplet is pronounced.

Moreover, the selection principle

$$\Delta S = 0$$

non longer applies since S is no longer a “good” conservation parameter (transition from $L-S$ for the $j-j$ coupling).

The table below gives the lines obtained by experiment:

Colour	λ/nm	Transition
yellow	581 ± 1	{ $6\,^1D1 \rightarrow 6\,^1P1$ $6\,^3D1 \rightarrow 6\,^1P1$
green	550 ± 1	$7\,^3S1 \rightarrow 6\,^3P1$
green	494 ± 2	$8\,^1S1 \rightarrow 6\,^1P1$
blue	437 ± 2	$7\,^1S \rightarrow 6\,^1P1$

Table 2: Measured spectral lines of Hg and the corresponding energy-level transitions.

Literature:

G. Herzberg, Atomic Spectra and Atomic Structure (Dover Publ.);
D. R. Bates, Quantum Theory II (Academic Press Inc.).