Separation of the centre of mass coordinates for an N-electron atom.

Razmotrimo atom (jon) koji sadrži nukleus mase M, naelektrisanje Ze, i N elektrona mase m. Obeležimo sa $\vec{R}_0$ radijus vektor nukleusa u odnosu na fiksni koord. početak 0, i $\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N$ za elektrone. Hamiltonijan za ovaj sistem je

$$H = T + V$$

$$T = -\frac{\hbar^2}{2M}\nabla_{R_0}^2 + \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_{R_i}^2\right)$$

V - pot. energija kao suma Kulonovih interakcija između $(N+1)$ čestice sistema

Da bi izdvojili kretanje centra mase uvedimo smenu $(\vec{R}_0, \vec{R}_1, \ldots, \vec{R}_N) \rightarrow (\vec{R}, \vec{r}_1, \ldots, \vec{r}_N)$

$$\vec{R} = \frac{1}{M+Nm}\left(M\vec{R}_0 + m\vec{R}_1 + \cdots + m\vec{R}_N\right)$$

$$\vec{r}_i = \vec{R}_i - \vec{R}_0, \quad i = 1, 2, \ldots, N$$

$$\Psi(\vec{R}_0, \vec{R}_1, \ldots, \vec{R}_N) \rightarrow \Psi(\vec{R}, \vec{r}_1, \ldots, \vec{r}_N)$$

$$\frac{\partial \psi}{\partial \vec{R}_0} = \frac{\partial \psi}{\partial \vec{R}}\frac{\partial \vec{R}}{\partial \vec{R}_0} + \sum_{i=1}^{N}\frac{\partial \psi}{\partial \vec{r}_i}\frac{\partial \vec{r}_i}{\partial \vec{R}_0}$$

tj. $\quad \nabla_{R_0} = \frac{\partial \vec{R}}{\partial \vec{R}_0}\nabla_R + \sum_{i=1}^{N}\frac{\partial \vec{r}_i}{\partial \vec{R}_0}\nabla_{r_i} = \frac{M}{M+Nm}\nabla_R - \sum_{i=1}^{N}\nabla_{r_i} \quad \cdots (1)$

$$\frac{\partial \psi}{\partial \vec{R}_1} = \frac{\partial \psi}{\partial \vec{R}}\frac{\partial \vec{R}}{\partial \vec{R}_1} + \sum_{i}\frac{\partial \psi}{\partial \vec{r}_i}\frac{\partial \vec{r}_i}{\partial \vec{R}_1}$$

$$\nabla_{R_1} = \frac{m}{M+Nm}\nabla_R + \nabla_{r_1}, \quad \text{tj.} \quad \nabla_{R_i} = \frac{m}{M+Nm}\nabla_R + \nabla_{r_i} \quad \cdots (2)$$

$$\nabla_{R_0}^2 = \left(\frac{M}{M+Nm}\right)^2\nabla_R^2 - \frac{2M}{M+Nm}\sum_{i=1}^{N}\nabla_R\cdot\nabla_{r_i} + \left(\sum_i\nabla_{r_i}\right)^2$$

$$\nabla_{R_i}^2 = \left(\frac{m}{M+Nm}\right)^2\nabla_R^2 + \frac{2m}{M+Nm}\nabla_R\cdot\nabla_{r_i} + \nabla_{r_i}^2$$

$$T = -\frac{\hbar^2}{2M}\left[\left(\frac{M}{M+N\mu}\right)^2 \nabla_R^2 - \frac{2M}{M+N\mu}\sum_i \nabla_R \cdot \nabla_{r_i} + \left(\sum \nabla_{r_i}\right)^2\right]$$

$$+ \sum_i \left\{-\frac{\hbar^2}{2\mu}\left[\left(\frac{\mu}{M+N\mu}\right)^2 \nabla_R^2 + \frac{2\mu}{M+N\mu}\nabla_R \cdot \nabla_{r_i} + \nabla_{r_i}^2\right]\right\}$$

$$= -\frac{\hbar^2}{2M}\frac{M + \mu\mu N}{(M+N\mu)^2}\nabla_R^2 - \frac{\hbar^2}{2}\left[-\frac{2}{M+N\mu} + \frac{2}{M+N\mu}\right]\sum \nabla_R \cdot \nabla_{r_i}$$

$$-\frac{\hbar^2}{2M}\sum \nabla_{r_i}^2 - \frac{\hbar^2}{2M} 2\sum_{i<j}\nabla_{r_i}\cdot\nabla_{r_j} - \frac{\hbar^2}{2\mu}\sum \nabla_{r_i}^2$$

$$T = -\frac{\hbar^2}{2(M+N\mu)}\nabla_R^2 - \frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\nabla_{r_i}^2 - \frac{\hbar^2}{M}\sum_{i<j}\nabla_{r_i}\cdot\nabla_{r_j}$$

$$\mu = \frac{\mu M}{M+\mu}$$

mass polarisation term

$$V(\vec{r_1}, \vec{r_2}, \ldots, \vec{r_N}) = -\sum_{i=1}^{N}\frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i<j}\frac{e^2}{(4\pi\varepsilon_0)\, r_{ij}}$$
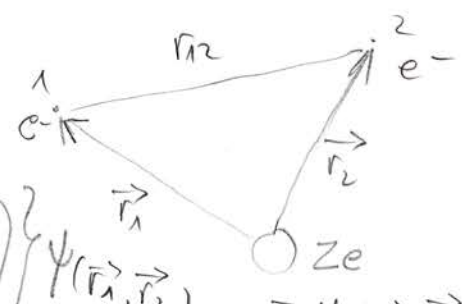
$$H\Psi_{tot}(\vec{R}, \vec{r_1}, \vec{r_2}, \ldots, \vec{r_N}) = E_{tot}\Psi_{tot}(\vec{R}, \vec{r_1}, \vec{r_2}, \ldots, \vec{r_N})$$

$$\Psi_{tot}(\vec{R}, \vec{r_1}, \ldots \vec{r_N}) = \Phi(\vec{R})\,\psi(\vec{r_1}, \vec{r_2}, \ldots \vec{r_N})$$

$$-\frac{\hbar^2}{2(M+N\mu)}\nabla_R^2 \Phi(\vec{R}) = E_{CM}\Phi(\vec{R})$$

$$\left[-\frac{\hbar^2}{2\mu}\sum_{i=1}^{N}\nabla_{r_i}^2 - \frac{\hbar^2}{\mu}\sum_{i<j}\nabla_{r_i}\cdot\nabla_{r_j} + V(\vec{r_1}\ldots\vec{r_N})\right]\psi = E\,\psi(r_1, \ldots r_N)$$

$$E_{tot} = E_{CM} + E$$

$$\left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \right\} \psi(\vec{r_1}, \vec{r_2}) = E\,\psi(\vec{r_1}, \vec{r_2})$$

Pod pretpostavkom da je $M = \infty$, ako nije, tačniji izraz bi bio:

$$\left[-\frac{\hbar^2}{2\mu}\nabla_{r_1}^2 - \frac{\hbar^2}{2\mu}\nabla_{r_2}^2 \underbrace{-\frac{\hbar^2}{M}\vec{\nabla}_{r_1}\cdot\vec{\nabla}_{r_2}}_{} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Zr^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \right] \psi(\vec{r_1},\vec{r_2}) = E\,\psi(\vec{r_1},\vec{r_2})$$

$\mu = \dfrac{m M}{m + M}$; $\qquad$ mass polarisation term

Zbog $\frac{1}{r_{12}}$ j-na nije separabilna i $\psi(\vec{r_1},\vec{r_2})$ se ne može napisati u vidu proizvoda jednoelektronskih t. f-ja.

T. f-je za sistem od dva ili više elektrona koje se ne mogu predstaviti kao single product of one-particle w.f. are said to be entangled. Odgovarajuća staya su entangled: merenje ne može biti urađeno na jednoj čestici bez uticaja druge.

Primetimo da gornje j-ne su nepromenjene ako se koordinate dva e^- promene. Neka je P_{12} an interchange operator

$$\psi(\vec{r_2}, \vec{r_1}) = P_{12}\,\psi(\vec{r_1}, \vec{r_2})$$

Ako t. f-je zadovoljavaju istu Šr. j-nu

$$\psi(\vec{r_2}, \vec{r_1}) = P_{12}\,\psi(\vec{r_1}, \vec{r_2}) = \lambda\,\psi(\vec{r_1}, \vec{r_2}) \qquad \text{primenim opet } P_{12}$$

$$P_{12}^2\,\psi(\vec{r_1},\vec{r_2}) = \lambda\,P_{12}\,\psi(r_1,r_2) = \lambda^2\,\psi(\vec{r_1},\vec{r_2}) = \psi(\vec{r_1},\vec{r_2})$$

$$\Rightarrow \lambda^2 = 1 ; \qquad \lambda = \pm 1$$

$$\psi(\vec{r_2}, \vec{r_1}) = \pm\,\psi(\vec{r_1}, \vec{r_2})$$

Simetričnost i antisimetričnost f-je izražava činjenicu da se čestice ne mogu razlikovati

$+ \rightarrow$ odgovara space-symmetric w. f. $\psi_+(\vec{r_1},\vec{r_2})$ or. para state
$- \rightarrow$ — ″ — — anti — $\psi_-(\vec{r_2},\vec{r_2})$ or. ortho state

Model nezavisnih čestica

Prost model koji daje mogućnost da kvalitativno računamo osnovne spektra (atomske jedinice)

$$H = H_0 + H'$$

$$H_0 = -\frac{1}{2}\nabla_{r_1}^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_2} = \hat{h}_1 + \hat{h}_2 \quad \left[\hat{h}_i = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right]$$
$$(i=1,2)$$

a perturbacija je $H' = \frac{1}{r_{12}}$

$$\hat{h}_i \psi_{n_i \ell_i m_i} = E_{n_i} \psi_{n_i \ell_i m_i} \quad ; \quad E_{n_i} = -\frac{1}{2}\frac{Z^2}{n_i^2}$$

$$H_0 \psi^{(0)}(\vec{r_1}, \vec{r_2}) = E^{(0)} \psi^{(0)}(\vec{r_1}, \vec{r_2})$$

$$\psi^{(0)}(\vec{r_1}, \vec{r_2}) = \psi_{n_1 \ell_1 m_1}(\vec{r_1}) \psi_{n_2 \ell_2 m_2}(\vec{r_2})$$

$$E^{(0)}_{n_1 n_2} = E_{n_1} + E_{n_2} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

— Osnovno stanje —

$$\psi_0^{(0)}(\vec{r_1}, \vec{r_2}) = \psi_{1s}(r_1)\psi_{1s}(r_2) = \frac{Z^3}{\pi}\exp\left[-Z(r_1 + r_2)\right]$$

$$E_0^{(0)} = E^{(0)}_{n_1=1, n_2=1} = -Z^2 \quad (a.u.) = -4\,a.u.\ (\simeq -108,8\,eV)$$

Prva popravka energije osnovnog stanja:

$$E_0^{(1)} = \langle \psi_0^{(0)} | H' | \psi_0^{(0)} \rangle = \int |\psi_{1s}(r_1)|^2 \frac{1}{r_{12}} |\psi_{1s}(r_2)|^2 \, d\vec{r_1}\,d\vec{r_2}$$

ili u SI sistem $E_0^{(1)} = \int |\psi_{1s}(r_1)|^2 \frac{e^2}{4\pi\varepsilon_0 r_{12}} |\psi_{1s}(r_2)|^2 \, d\vec{r_1}\,d\vec{r_2}$

Interpretacija: $|\psi_{1s}(r_1)|^2$ gustina v-će nalaženja e "1" u $\vec{r_1}$

$\rho(r_1) = -e|\psi_{1s}(r_1)|^2$ gustina naelektrisanja zbog elektrona 1

$\rho(r_2) = -e|\psi_{1s}(r_2)|^2$ — '' — 2

$\Rightarrow$ gornji integral je elektrostatička interakciona energija of two overlapping spherically symmetric distributions of electricity.

$$E_0^{(1)} = \frac{Z^6}{\pi^2} \int \exp[-2Z(r_1+r_2)] \frac{1}{r_{12}} d\vec{r_1} d\vec{r_2}$$
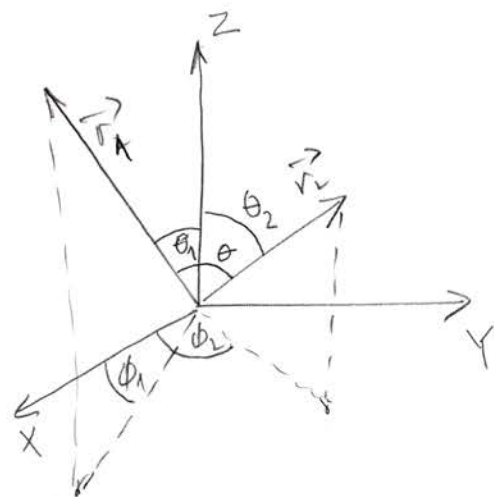
Za rešavanje koristićemo generalnu proceduru koja je veoma korisna u atomskoj fizici.

Razvijmo $\frac{1}{r_{12}}$ u Legendreove polinome:

$$\frac{1}{r_{12}} = \frac{1}{r_1} \sum_{\ell=0}^{\infty} \left(\frac{r_2}{r_1}\right)^{\ell} P_{\ell}(\cos\theta), \quad r_1 > r_2$$

$$= \frac{1}{r_2} \sum_{\ell=0}^{\infty} \left(\frac{r_1}{r_2}\right)^{\ell} P_{\ell}(\cos\theta), \quad r_1 < r_2.$$

gde je θ ugao između $\vec{r_1}$ i $\vec{r_2}$ tako doje:

$$\cos\theta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1-\phi_2)$$

ili u kompaktnoj formi:

$$\frac{1}{r_{12}} = \sum \frac{(r_<)^{\ell}}{(r_>)^{\ell+1}} P_{\ell}(\cos\theta)$$

$r_<$ manje od r_1, r_2 a $r_>$ veće

Koristeći adicionu teoremu za sferne harmonike:

$$\frac{1}{r_{12}} = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{4\pi}{2\ell+1} \frac{(r_<)^{\ell}}{(r_>)^{\ell+1}} Y_{\ell m}^*(\theta_1,\phi_1) Y_{\ell m}(\theta_2,\phi_2)$$

jer je $P_{\ell}(\cos\theta) = \frac{4\pi}{2\ell+1} \sum_{m=-\ell}^{+\ell} Y_{\ell m}^*(\theta_1,\phi_1) Y_{\ell m}(\theta_2,\phi_2)$

Koristeći $Y_{00} = \frac{1}{\sqrt{4\pi}}$ imamo:

$$E_0^{(1)} = \frac{Z^6}{\pi^2} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{(4\pi)^2}{2\ell+1} \int_0^{\infty} dr_1 r_1^2 \int_0^{\infty} dr_2 r_2^2 \exp[-2Z(r_1+r_2)] \frac{(r_<)^{\ell}}{(r_>)^{\ell+1}} \times$$

$$\times \int d\Omega_1 Y_{\ell m}^*(\theta_1,\phi_1) Y_{00} \int d\Omega_2 Y_{00} Y_{\ell m}(\theta_2,\phi_2)$$

$$= \frac{Z^6}{\pi^2} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \frac{(4\pi)^2}{2\ell+1} \int_0^{\infty} dr_1 r_1^2 \int_0^{\infty} dr_2 r_2^2 \exp[-2Z(r_1+r_2)] \frac{(r_<)^{\ell}}{(r_>)^{\ell+1}} \delta_{\ell,0} \delta_{m0}$$
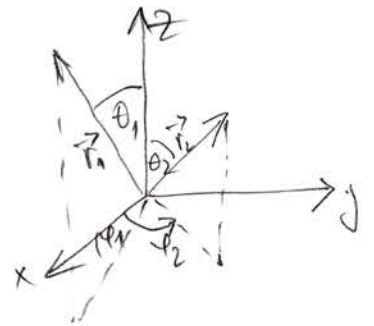
$\frac{1}{r_{12}}$ može da se razvije preko Legendre-ovih polinoma

$$\frac{1}{r_{12}} = \begin{cases} \frac{1}{r_1} \sum\limits_{l=0}^{\infty} \left(\frac{r_2}{r_1}\right)^l P_l(\cos\theta), & r_1 > r_2 \\ \frac{1}{r_2} \sum\limits_{l=0}^{\infty} \left(\frac{r_1}{r_2}\right)^l P_l(\cos\theta), & r_1 < r_2 \end{cases}$$

θ ugao izmedju $\vec{r_1}$ i $\vec{r_2}$: $\cos\theta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\varphi_1 - \varphi_2)$

Ovo može da se zapiše i ovako

$$\frac{1}{|\vec{r_1} - \vec{r_2}|} = \frac{1}{r_{12}} = \sum\limits_{l=0}^{\infty} \frac{(r_<)^l}{(r_>)^{l+1}} P_l(\cos\theta)$$

Koristeći 'addition theorem'

$$P_l(\cos\theta) = \frac{4\pi}{2l+1} \sum\limits_{m=-l}^{+l} Y_{lm}^*(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

$$\frac{1}{r_{12}} = \sum\limits_{l=0}^{\infty} \sum\limits_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{(r_<)^l}{(r_>)^{l+1}} Y_{lm}^*(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

Može da se pokaže i ovo [BJ. p.614]

$$\frac{e^{ik|\vec{r_1} - \vec{r_2}|}}{|\vec{r_1} - \vec{r_2}|} = ik \sum\limits_{l=0}^{\infty} (2l+1) j_l(kr_<) \left[j_l(kr_>) + i n_l(kr_>) \right] P_l(\cos\theta)$$

j_l i n_l sferna Beselova i Neumann-ova f-ja.

i na kraju treba znati i ovaj razvoj

$$e^{i\vec{k}\cdot\vec{r}} = \sum\limits_{l=0}^{\infty} (2l+1) i^l j_l(kr) P_l(\cos\theta)$$

Svi sabirci dvostruce sume biće nula izuzev $\ell = m = 0$

$$E_0^{(1)} = 16 Z^6 \int_0^\infty dr_1 r_1^2 \int_0^\infty dr_2 r_2^2 \exp[-2Z(r_1+r_2)] \frac{1}{r_>}$$

$$= 16 Z^6 \int_0^\infty dr_1 r_1^2 \exp(-2Zr_1)\left[\frac{1}{r_1} \int_0^{r_1} dr_2 r_2^2 \exp(-2Zr_2) + \int_{r_1}^\infty dr_2 r_2 \exp(-2Zr_2) \right]$$

sada se lako radi i rešenje je

$$E_0^{(1)} = \frac{5}{8} Z \quad a.u.$$

Pazili smo na dva dela

$$\frac{1}{r_{12}} = \frac{1}{r_1} \quad , \quad r_1 > r_2$$

$$\frac{1}{r_{12}} = \frac{1}{r_2} \quad \quad r_2 > r_1$$

Za prevo, dvostruca suma $\frac{1}{r_{12}}$ za $\ell = m = 0$ to postaje

ili u SI sistemu:

$$E_0^{(1)} = \frac{5}{8}\left(\frac{e^2}{4\pi\varepsilon_0}\right) \frac{Z}{a_0}$$

Kako je He ; $Z = 2$ $\qquad E_0^{(1)} \approx 34\,eV = E_{1s^2}^{Z=2}$

	$-E_0^{(0)}$ [ev]	$-E^{calc} \approx E_0^{(0)} + E^{(1)}$ [ev]	$-E^{EXP.}$ [ev]	$\left\|\frac{E^{calc} - E^{EXP}}{E^{EXP}}\right\|$ %
He	108,76	74,78	78,98	5,3
Li$^+$	244,71	193,73	198,04	2,2
Be^{++}	435,04	367,06	371,51	1,2
B^{3+}	679,75	594,78	599,43	0,8
C^{4+}	978,84	876,88	881,83	0,6

Vidimo da teorija, koristeći samo prvu aproksimaciju, daje dosta dobro slaganje računskih vrednosti sa eksperimetalnim. Očiglodno je slaganje bolje ukoliko je redni broj elementa viši.

Napomena:

Drugi način rešavanja integrala može ovako:
uzmemo z-osu duž vektora položaja $\vec{r_1}$ pa je onda:

$$r_{12} = \sqrt{r_1^2 + r_2^2 - 2\,r_1 r_2 \cos\theta}$$

onda integracija po θ_1 može da se izvede pomoću:

$$\int \frac{\sin\theta_1\,d\theta_1}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos\theta_1}} = \begin{cases} \dfrac{4}{r_2} & \text{za } r_1 < r_2 \\ 0, & r_1 > r_2 \end{cases}$$

Primena teorije perturbacije uz popravke drugog reda
nailazi na nepraktična glomazna izračunavanja. Dalja
precizna izračunavanja dobijaju se drugim aproksimacijama
prvenstveno varijacionom metodom. ⟵ Sada uvodi varij. metod.

$$\Psi(\vec{r_1}, \vec{r_2}) = \frac{\lambda^3}{\pi} e^{-\lambda(x_1 + x_2)} \qquad \lambda = 1{,}6875 \qquad \text{Hylleraas w. f.}$$
$$\lambda = Z - \frac{5}{16}$$

$$\Psi(x_1, x_2) = \frac{N}{\pi}\left(e^{-\alpha_1 x_1 - \alpha_2 x_2} + e^{-\alpha_2 x_1 - \alpha_1 x_2}\right) \Bigg\} \quad \text{Silverman et. al. w. f.}$$
$$N = \left[\frac{1}{\alpha_1^3} + \frac{1}{\alpha_2^3} + \frac{16}{(\alpha_1 + \alpha_2)^3}\right]^{-1/2} \quad \text{[Chandrasekhar]}$$

Multi parameter (12-108), highly correlated w. f. of
Joachain and Vanderpoorten a isti oblik imaju
f-je Byron and Joachain

$$\Psi(\vec{x_1}, \vec{x_2}) = \sum_{\ell=0}^{L} R_\ell(x_1, x_2)\, P_\ell(\hat{\vec{X_1}} \cdot \hat{\vec{X_2}})$$

$$R_\ell(x_1, x_2) = \frac{1}{4\pi} \sum_{nn'} A^{(\ell)}_{nn'}\left[x_1^{n+\ell} x_2^{n'+\ell} e^{-\frac{1}{2}(\alpha x_1 + \beta x_2)} + (1 \leftrightarrow 2)\right]$$

$A^{(\ell)}_{nn'}, \alpha, \beta \rightarrow$ parametri.

F-je Tweed-a (od 21 do 41 parametr) su istog oblika samo
nemaju $(x_1 x_2)^\ell$ /Drake NIMB (1996)

$$E = -2{,}903724377034119598 13 \text{ au.}$$

Varijacioni metod

Probna $\Psi(\vec{r_1}, \vec{r_2}) = \Psi_1(\vec{r_1})\,\Psi_2(\vec{r_2}) = \frac{1}{\pi}\frac{Z_e^3}{a^3}\, e^{-\frac{Z_e r_1}{a}}\, e^{-\frac{Z_e r_2}{a}}$
fja:

Z_e - efektivno naelektrisanje tretirano kao varijacioni parametr.

Srednja vrednost energije

$$\overline{E} = \int \Psi^* \hat{H}\, \Psi \, d\tau$$

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$\Psi_1(\vec{r_1})$ i $\Psi_2(\vec{r_2})$ su rešenja za jednoelektronske atome

$$-\frac{\hbar^2}{2m}\nabla_1^2 \Psi_1(\vec{r_1}) = \frac{1}{4\pi\varepsilon_0}\frac{Z_e e^2}{r_1}\Psi_1(\vec{r_1}) + Z_e^2 E_H \, \Psi_1(\vec{r_1})$$

$$-\frac{\hbar^2}{2m}\nabla_2^2 \Psi_2(\vec{r_2}) = \frac{1}{4\pi\varepsilon_0}\frac{Z_e e^2}{r_2}\Psi_2(\vec{r_2}) + Z_e^2 E_H \, \Psi_2(\vec{r_2})$$

$$Z_e^2 E_H = -\frac{m Z_e^2 e^4}{(4\pi\varepsilon_0)^2 2\hbar^2} = Z_e^2\left(-\underbrace{\frac{e^2}{(4\pi\varepsilon_0)2a}}_{E_H}\right)$$

$$\Rightarrow \hat{H} = \frac{1}{4\pi\varepsilon_0}\frac{Z_e e^2}{r_1} + Z_e^2 E_H + \frac{1}{4\pi\varepsilon_0}\frac{Z_e e^2}{r_2} + Z_e^2 E_H - \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$= 2 Z_e^2 E_H + \frac{e^2}{4\pi\varepsilon_0}(Z - Z_e)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\overline{E} = 2 Z_e^2 E_H + \frac{e^2}{4\pi\varepsilon_0}(Z - Z_e)\underbrace{\int \Psi_1^*(\vec{r_1})\Psi_2^*(\vec{r_2})\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\Psi_1(\vec{r_1})\Psi_2(\vec{r_2})\,d\tau_1\,d\tau_2}_{I_1}$$

$$+ \frac{e^2}{4\pi\varepsilon_0}\underbrace{\int \Psi_1^*(\vec{r_1})\Psi_2^*(\vec{r_2})\frac{1}{r_{12}}\Psi_1(\vec{r_1})\Psi_2(\vec{r_2})\,d\tau_1\,d\tau_2}_{I_2}$$

$$I_1 = \underbrace{\int \psi_1^2(\vec{r_1}) \frac{1}{r_1} d\tau_1 \int \psi_2^2(\vec{r_2}) d\tau_2}_{=1} + \underbrace{\int \psi_1^2(\vec{r_1}) d\tau_1 \int \psi_2^2(\vec{r_2}) \frac{1}{r_2} d\tau_2}_{=1} \quad r_2 \to r_1$$

$$= 2 \int \psi_1^2(\vec{r_1}) \frac{1}{r_1} d\tau_1 = \frac{2Ze^3}{\pi a^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{r_1} e^{-\frac{2Ze\,r_1}{a}} r_1^2 dr_1 \, d\varphi_1 \sin\theta_1 d\theta_1$$

$$I_1 = \frac{2Ze}{a}$$

Drugi integral smo već izračunali

$$I_2 = \frac{5}{8} \frac{Ze}{a}$$

$$E_H = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{2a}$$

$$\Rightarrow \bar{E} = 2Z_e^2 E_H + \frac{e^2(Z_e - Z)}{4\pi\epsilon_0} \frac{2Ze}{a} + \frac{e^2}{4\pi\epsilon_0} \frac{5}{8} \frac{Ze}{a} = \left[2Z_e^2 - 4Z_e(Z_e - Z) - \frac{5}{4} Z_e \right] E_H$$

$$\frac{\partial \bar{E}}{\partial Z_e} = \left(4Z_e - 8Z_e + 4Z - \frac{5}{4} \right) E_H = 0$$

$$\Rightarrow \boxed{Z_e = Z - \frac{5}{16}}$$

$$E_{min} = 2\left(Z - \frac{5}{16}\right)^2 E_H = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{a} \left(Z - \frac{5}{16}\right)^2$$

Razvijmo dobijeni izraz:

$$E = -\frac{1}{4\pi\epsilon_0} \frac{Z^2 e^2}{a} + \underbrace{\frac{1}{4\pi\epsilon_0} \frac{5}{8} \frac{Ze^2}{a}}_{\text{ovo daje teorija perturbacy}} - \frac{e^2}{4\pi\epsilon_0 a} \left(\frac{5}{16}\right)^2$$

Razlika
(efikasnost)

$$\Delta E = 2\left(\frac{5}{16}\right)^2 E_H \quad \text{ne zavisi od } Z$$

The integrals are now straightforward, and yield the answer

$$E_0^{(1)} = \tfrac{5}{8}Z \quad \text{a.u.} \tag{6.65}$$

which is a positive contribution to the energy, as expected. We also remark that $E_0^{(1)}$ is linear in Z [2], while the unperturbed energy $E_0^{(0)} = -Z^2$ a.u. is quadratic in Z, so that the ratio $|E_0^{(1)}/E_0^{(0)}|$ decreases like Z^{-1} when Z increases. This is in line with our comments in the previous section concerning the decrease in relative importance of the electron-electron repulsion term $1/r_{12}$ with increasing Z.

Adding the first-order correction [6.65] to our zero-order result $E_0^{(0)} = -Z^2$ a.u., we find for the ground state energy E_0 the approximate value

$$E_0 \simeq E_0^{(0)} + E_0^{(1)} = -Z^2 + \tfrac{5}{8}Z \quad \text{a.u.} \tag{6.66}$$

Both this 'first-order' result and the unperturbed energy $E_0^{(0)}$ are given in Table 6.3 for various two-electron atoms (ions), from the negative hydrogen ion H$^-$ ($Z = 1$) to four times ionised carbon C^{4+} ($Z = 6$). The 'exact' [3] values E_0^{ex} are also tabulated. Except for H$^-$, the simple first-order perturbation approach yields quite good results. If we define ΔE, where

$$\Delta E = E_0^{ex} - (E_0^{(0)} + E_0^{(1)}) \tag{6.67}$$

Table 6.3 Values of the ground state energy E_0 of the Hamiltonian [6.2], for various two-electron atoms and ions (in atomic units)

	Unperturbed $E_0^{(0)}$	Ground state energy		'Exact'
		First order $E_0^{(0)} + E_0^{(1)}$	Simple variational $\left(Z_e = Z - \dfrac{5}{16}\right)$	
	(equation [6.37])	(equation [6.66])	(equation [6.79])	
H$^-$	-1	-0.375	-0.473	-0.528
He	-4	-2.750	-2.848	-2.904
Li$^+$	-9	-7.125	-7.222	-7.280
Be^{2+}	-16	-13.50	-13.60	-13.66
B^{3+}	-25	-21.88	-21.97	-22.03
C^{4+}	-36	-32.25	-32.35	-32.41

[2] The fact that $E_0^{(1)}$ is linear in Z may readily be understood by noting that each charge distribution in [6.56] contains a total charge $-e$ and extends over a region of space of linear dimension given approximately by $a = a_0/Z$. Their mutual interaction energy is therefore roughly given by $e^2/(4\pi\epsilon_0)a = Ze^2/(4\pi\epsilon_0)a_0$, which is indeed proportional to Z.

[3] The 'exact' results quoted in Table 6.3 are accurate values of the ground state energy E_0 of the Hamiltonian [6.2], obtained by using the Rayleigh–Ritz variational method with elaborate trial functions. Only a few of the presently available significant figures are given. Since these 'exact' values of E_0 must still be corrected for the motion of the nucleus, as well as relativistic and radiative corrections, they should not be confused with the experimental ground state energies E_0^{exp}.

as the difference between the 'exact' value E_0^{ex} and the first-order result [6.66], we see that the ratio $|\Delta E/E_0^{ex}|$ varies from about 5 per cent for He to 0.4 per cent for C^{4+}. It is interesting to note that this first-order perturbation treatment, carried out by Unsöld in 1927, was the first quantum mechanical calculation of the helium ground state. In view of the large discrepancies shown by the old quantum theory calculations, the relatively small difference of about 0.15 a.u. (≈ 4 eV) between his result and the experimental value was very promising.

The calculation of second and higher order corrections, $E_0^{(n)}$ ($n \geq 2$), is a much more difficult problem, to which we shall return further, after having discussed the Rayleigh–Ritz variational approach.

Variational method

We have seen in Section 2.8 that if H denotes the Hamiltonian of a quantum system, and ϕ a physically admissible trial function, the functional

$$E[\phi] = \frac{\langle \phi|H|\phi \rangle}{\langle \phi|\phi \rangle} \tag{6.68}$$

provides a variational principle for the discrete eigenvalues of the Hamiltonian. Moreover, it also yields a minimum principle for the ground state energy. That is,

$$E_0 \leq E[\phi] \tag{6.69}$$

For the case of two-electron atoms the Hamiltonian H (neglecting the motion of the nucleus and all but the Coulomb interactions) is given by [6.2]. Following the Rayleigh–Ritz variational method, we shall use trial functions ϕ depending on variational parameters, and carry out the variation $\delta E = 0$ with respect to these parameters.

It is apparent from the discussion of Section 6.4 that a basic defect of the 'zero-order' ground state wave function [6.35] (from which the first-order energy result [6.66] was obtained) is that each electron moves in the fully unscreened field of the nucleus. In order to take into account approximately the screening effect of each electron on the other one, we shall therefore choose a trial function of the form [6.47]. That is, (in a.u.)

$$\phi(r_1, r_2) = \frac{Z_e^3}{\pi} e^{-Z_e(r_1+r_2)} \tag{6.70}$$

or

$$\phi(r_1, r_2) = \psi_{1s}^{Z_e}(r_1)\psi_{1s}^{Z_e}(r_2) \tag{6.71a}$$

where

$$\psi_{1s}^{Z_e}(r) = \left(\frac{Z_e^3}{\pi}\right)^{1/2} e^{-Z_e r} \tag{6.71b}$$

and the 'effective charge' Z_e is considered as a variational parameter.

Pobuđena stanja

Za početak razmotrimo jednostruko pobuđena stanja
Simetrizovana prostorna f-ja nultog reda biće

$$\Psi_\pm^{(0)}(\vec{r_1},\vec{r_2}) = \frac{1}{\sqrt{2}}\left[\psi_{100}(\vec{r_1})\psi_{nlm}(\vec{r_2}) \pm \psi_{nlm}(\vec{r_1})\psi_{100}(\vec{r_2})\right]$$

$$E_{1,n}^{(0)} = -\frac{Z^2}{2}\left(1+\frac{1}{n^2}\right) \quad a.u. \quad n \geq 2 \quad \left|\begin{array}{l} + \text{ para} \\ - \text{ orto}\end{array}\right.$$

Prva popravka [za degenerisanot vidi B.J. p.339>

$$E_\pm^{(1)} = \langle \psi_\pm^{(0)}|H'|\psi_\pm^{(0)}\rangle \quad ; \qquad H' = \frac{1}{r_{12}}$$

$$E_+^{(1)} = J + K \quad ; \qquad E_-^{(1)} = J - K$$

gde je $J = \int |\psi_{100}(\vec{r_1})|^2 \frac{1}{r_{12}} |\psi_{nlm}(\vec{r_2})|^2 d\vec{r_1}d\vec{r_2}$ $\begin{bmatrix}\text{Coulomb-ov ili}\\ \text{direktni integral}\end{bmatrix}$

$$K = \int \psi_{100}^*(\vec{r_1})\psi_{nlm}^*(\vec{r_2}) \frac{1}{r_{12}} \psi_{100}(\vec{r_2})\psi_{nlm}(\vec{r_1}) d\vec{r_1}d\vec{r_2} \begin{bmatrix}\text{exchange}\\ \text{integral}\end{bmatrix}$$

Kako je $\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta,\varphi)$ i koristeći
ortonormiranost sf. harmonika i razvoj za $\frac{1}{r_{12}}$ imamo:

$$J_{nl} = \int_0^\infty dr_2\, r_2^2\, R_{nl}^2(r_2)\int_0^\infty dr_1\, r_1^2\, R_{10}^2(r_1)\frac{1}{r_>}$$

$$K_{nl} = \frac{1}{2l+1}\int_0^\infty dr_2\, r_2^2\, R_{10}(r_2)R_{nl}(r_2)\int_0^\infty dr_1\, r_1^2\, R_{10}(r_1)R_{nl}(r_1)\frac{(r_<)^l}{(r_>)^{l+1}}$$

gde smo naglasili da ai integrali zavise od nil a ne i od m

$$E_{nl\pm}^{(1)} = J_{nl} \pm K_{nl}$$

$$E_{nl,\pm} = E_{1,n}^{(0)} + E_{nl\pm}^{(1)} \simeq -\frac{Z^2}{2}\left(1+\frac{1}{n^2}\right) + J_{nl} \pm K_{nl} \qquad (*)$$

Integrali J_{nl} i K_{nl} mogu da se izračunaju eksplicitno, ovde ćemo
navesti samo važne osobine. Pre svega J_{nl} mora biti pozitivno.
Međutim, i $K_{nl} > 0$ tako da sledi iz (*) orto stanje (tripletno) imaju nižu
energiju od odgovarajućeg para (singlet) stanje što ima iste vrednosti ni...
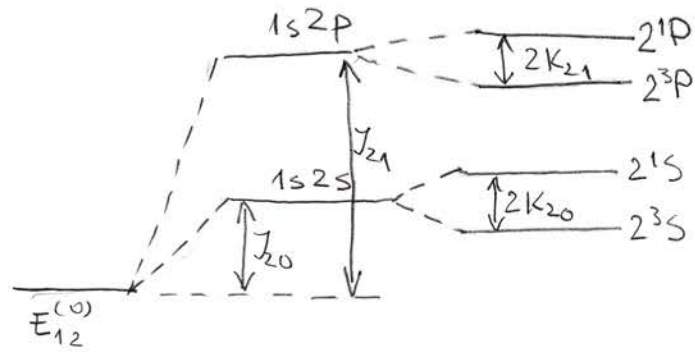
Radijativni prelaz između singletnog i tripletnog spinskog stanja (pozvat kao interkombinacione linije) je **zabranjen** u dipolnoj aproksimaciji, s tim što spin-orbitalna interakcija se može zanemariti. To je slučaj sa atomima i jonima sa niskim Z, tako da energ. spektar dvoelekt. atoma (jona) sa Z≲40 sadrži **dva približno nezavisna sistema nivoa: para i orto.** (vidi sliku)

Spektar dvoel. jona sa Z>2 je veoma sličan He-atomu. Sa druge strane negativni jon H⁻ ima **samo jedno** vezano stanje. Jonizac. potencijal je 0,75 eV u odnosu na detachment u neutralni H i slobodan e⁻.

$E(eV)$ 0 ////////////////////// $H(1s)+e^-$

$-0,75$ ———————————— $H^-(^1S)$
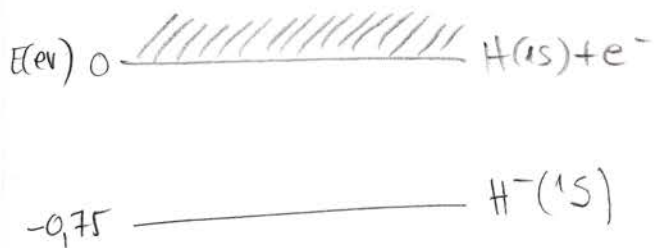
Dvostruko pobuđena stanja

To su stanja kada su oba e⁻ pobuđena npr. $2s^2$, $2s2p$, $3p4d$...
Napomenimo da sva ova stanja leže iznad jonizacionog
praga i zbog toga diskretna stanja embedded
(ubačen)
in the continuum. Tu se dešava radiationless transitions
iz dvostruko pobud. stanje na stanje jonizovane konfiguracije
Takav prelaz je Auger-ov ili autojonizacioni, i
dvostruko pobud. staja (koja su nestabilna u odnosu
na jonizaciju) se nazivaju autojonizaciona stanja

[B.J. p. 345]

Spinska stanja sa dva e^- mogu biti 4 f-je stanja

$$\alpha(1)\,\alpha(2) \qquad\qquad \alpha(1)\,\beta(2)$$
$$\beta(1)\,\beta(2) \qquad\qquad \beta(1)\,\alpha(2)$$

Osim te 4 moguće su i linearne kombinacije ovih 4 f-ja.. Stanja $\alpha(1)\alpha(2)$ i $\beta(1)\beta(2)$ su simetrična a od stanja $\alpha(1)\beta(2)$ i $\beta(1)\alpha(2)$ možemo napraviti stanja koja će uvek biti simetrična ili antisimetrična

$$\alpha(1)\beta(2) + \alpha(2)\beta(1) \rightarrow \text{simetrična}$$
$$\alpha(1)\beta(2) - \alpha(2)\beta(1) \rightarrow \text{antisimetrična}.$$

ukupni m_S koji opisuje ove dve poslednje f-je je $\emptyset$ a za stanja $\alpha(1)\alpha(2)$ je $+1$, dok za $\beta(1)\beta(2)$ -1

F-ja stanja spina	$M_S = m_S(1) + m_S(2)$	S
$\alpha(1)\,\alpha(2)$	$+1$	
$\alpha(1)\beta(2) + \alpha(2)\beta(1)$	0	$\Big\}\ 1$
$\beta(1)\beta(2)$	-1	
$\alpha(1)\beta(2) - \alpha(2)\beta(1)$	0	0

$$\alpha(1)\,\alpha(2) \rightarrow m_S(1) + m_S(2) = \tfrac{1}{2} + \tfrac{1}{2} = 1$$
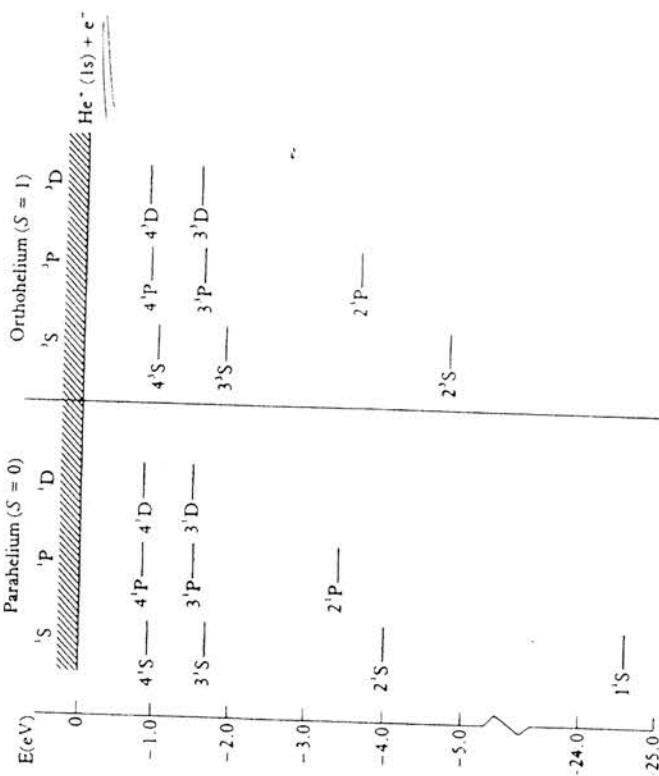$$\beta(1)\,\beta(2) \rightarrow m_S(1) + m_S(2) = -\tfrac{1}{2} - \tfrac{1}{2} = -1$$
$$\alpha(1)\,\beta(2) \rightarrow m_S(1) + m_S(2) = +\tfrac{1}{2} - \tfrac{1}{2} = \emptyset$$
$$\beta(1)\,\alpha(2) \rightarrow m_S(1) + m_S(2) = -\tfrac{1}{2} + \tfrac{1}{2} = \emptyset$$

Spectroskopski označavamo stanje ^{2S+1}L tako da imamo singletno stanje $S = 0$ i tripletno $(S=1)$

two-electron atoms

6.3

Parahelium (S = 0)   Orthohelium (S = 1)

He⁺(1s) + e⁻

| ¹S | ¹P | ¹D | | ³S | ³P | ³D |

E(eV)

0 —

−1.0 — 4¹S 4¹P 4¹D   4³S 4³P 4³D
−2.0 — 3¹S 3¹P 3¹D   3³S 3³P 3³D
−3.0 —
            2¹P   2³P
−4.0 — 2¹S
                           2³S
−5.0 —

−24.0 —

−25.0 — 1¹S

The experimental values of the lowest energy levels of helium. The energy scale is chosen so that 0 corresponds to the ionisation threshold. The configuration of each level is of the form 1s nl. doubly excited states (for example 2s nl) are at positive energies on this scale, within the (1s) + e⁻ continuum.
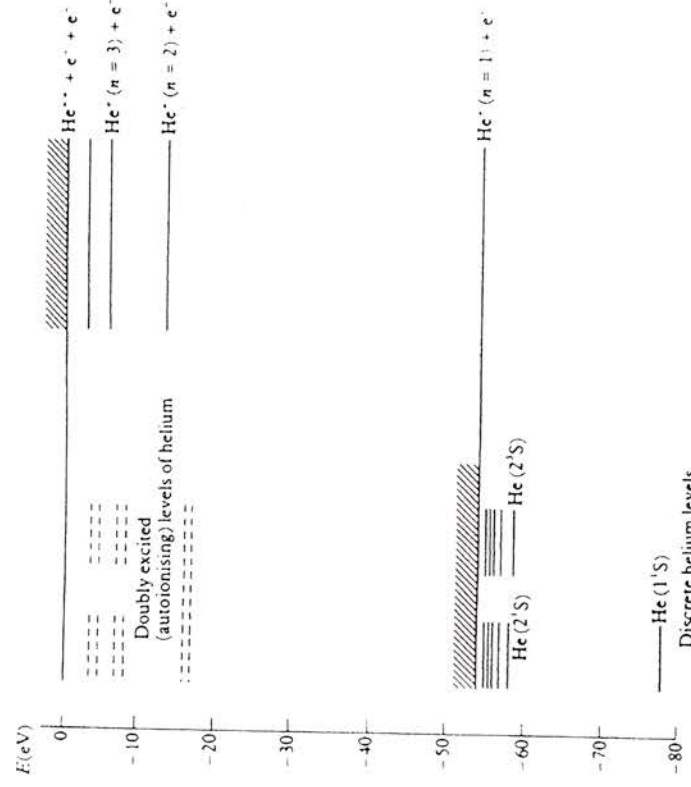
so on. In addition, a superscript to the left gives the value of the quantity + 1, or *multiplicity*, which is equal to 1 for singlet (S = 0) states and 3 for let (S = 1) states.

We remark that Fig. 6.2 does not exhibit the fine structure splitting of the ls, due to the relativistic interaction between the spin and orbital angular nentum (spin–orbit effect) and to the magnetic interaction between the s of the two electrons (spin–spin effect). Calling $J = L + S$ the total elec- ic angular momentum and denoting by $J(J + 1)$ and M_J the eigenvalues of the operators J^2 and J_z, respectively, it may be shown that the spin–orbit spin–spin interactions partially remove the degeneracy of the triplet states plitting them (except the ³S states) into three closely spaced levels corre- ding to the three possible values $J = L + 1, L$ or $L - 1$ of the total angular nentum quantum number J. We shall discuss this problem in Chapter 8. should be noted that Fig. 6.2 only represents the *discrete* part of the three- trum. A schematic diagram of the 'full' spectrum for the three-body system isting of the He⁺⁺ nucleus and two electrons is shown in Fig. 6.3. Choos- the origin of the energy scale in such a way that all three particles are

---

Level scheme of two-electron atoms

6.3

He⁺⁺ + e⁻ + e⁻
He⁺(n = 3) + e⁻
He⁺(n = 2) + e⁻

Doubly excited (autoionising) levels of helium

He⁺(n = 1) + e⁻

He(2¹S)

He(2³S)   He(2¹S)

He(1¹S)

Discrete helium levels

E(eV) 0 —, −10, −20, −30, −40, −50, −60, −70, −80

6.3 The 'complete' energy level spectrum of helium. The energy scale is relative to the threshold for the ionisation of both electrons and the zero of energy is 54 eV (the ground state energy of He⁺), above the zero energy of the scale of Fig. 6.2.

unbound above $E = 0$, we see that the discrete levels of helium (displayed in more detail in Fig. 6.2) lie between the ground state value $E_0(\text{He}) = -79.0$ eV and the value $E_0(\text{He}^+) = -54.4$ eV of the ground state energy of the He⁺ ion. Thus the ionisation potential numbers given in Fig. 6.2 correspond to the energy differences between the level $E_0(\text{He}^+)$ and a given energy level of the helium atom. For example, the ionisation potential corresponding to the helium ground state is

$$I_P = E_0(\text{He}^+) - E_0(\text{He})$$
$$= 24.6 \text{ eV} \qquad [6.22]$$

The spectrum of two-electron ions with $Z > 2$ is similar to that of helium which we have just discussed. On the other hand, the negative hydrogen ion H⁻, for which $Z = 1$, constitutes an interesting special case. Indeed, as shown on Fig. 6.4, this ion has only *one* bound state. The corresponding ionisation potential is about 0.75 eV, so that the H⁻ ion is barely stable against dissociation into a neutral hydrogen atom and a free electron. We shall return
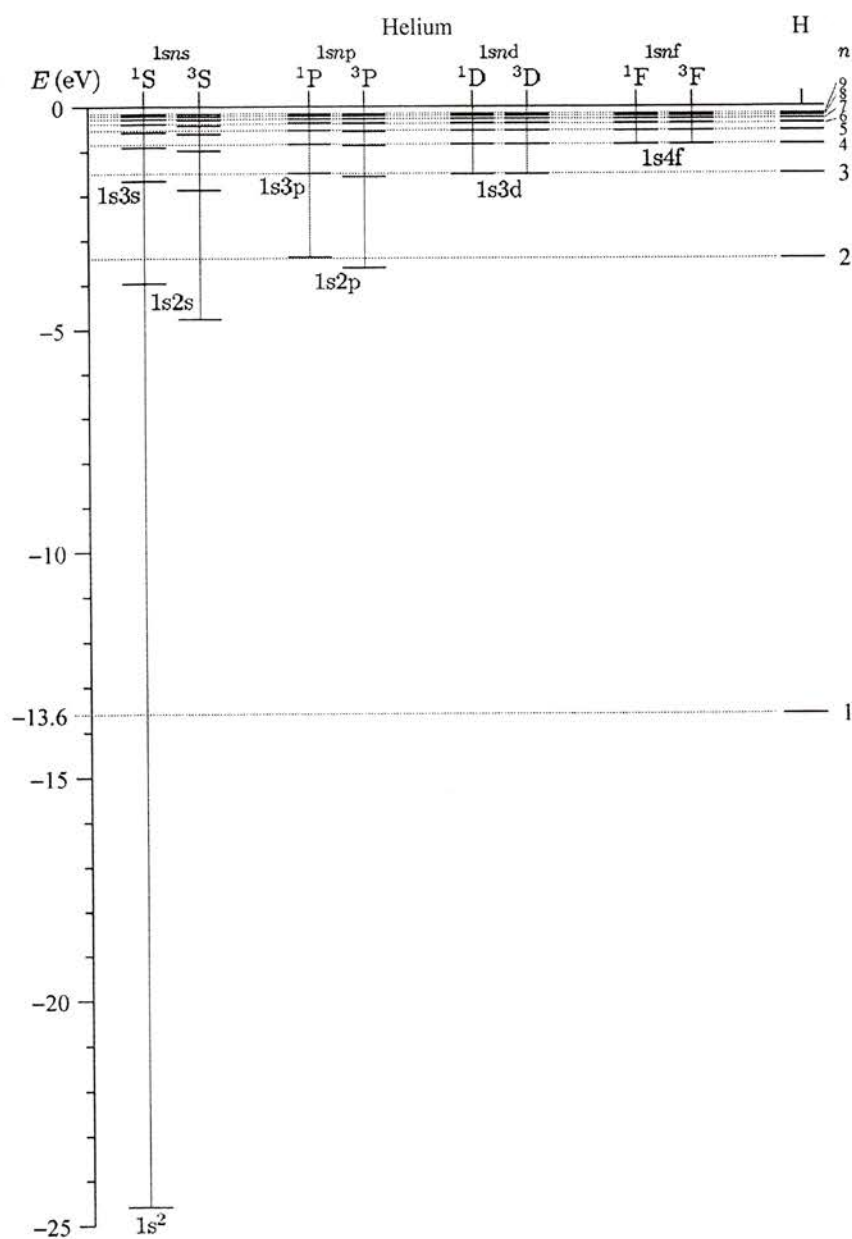
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Fig. 3.4 The energy levels of the helium atom with those of hydrogen for comparison. The $1s^2$ ground configuration is tightly bound. For the excited configurations of helium the 1s-electron screens the outer electron from the nuclear charge so that the $1snl$ configurations in helium have similar energy to the shell with principal quantum number n in hydrogen. The hydrogenic levels are indicated on the right. The interval between the ^1L and ^3L terms (equal to twice the exchange integral) is clear for the 1s2s, 1s2p, 1s3s, 1s3p and 1s4s configurations but it is smaller for higher n and l.