1) $\hat{\mathcal{H}}_1 = \frac{\hat{p}^2}{2m} + \hat{h}$ $\qquad \hat{h} \text{ "=" } \sum_\alpha \left(\frac{\vec{\pi}_\alpha^2}{2\mu_\alpha} + v(\vec{\rho}_\alpha) \right) \overset{\text{obecně}}{=} \hat{h}(\vec{\pi}_\alpha, \vec{\rho}_\alpha)$;

$\uparrow$ klas $\qquad\qquad \uparrow$ kvant $\Rightarrow$ spektrum ϵ_q, $q = 0, \dots, \infty$

2) $\Rightarrow \Omega(T,V,\mu) = -kTV \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \xi(T) e^{\mu/kT}$

3) $pV = NkT$

4) $U(T) = \frac{3}{2}NkT + NkT^2 \frac{d}{dT} \log \xi(T)$

$$\Rightarrow C_V = \frac{3}{2}Nk + Nk\frac{d}{dT}\left(T^2 \frac{d}{dT} \log \xi\right) = \frac{3}{2}Nk + 2NkT^2\frac{d}{dT}\log\xi(T) + NkT^2 \frac{d^2}{dT^2}\log \xi(T)$$

5) $C_p = C_V + Nk \Leftarrow H = U + pV = U + NkT$

$\Leftarrow S(T,V) \to S(T,p) \Rightarrow T\left(\frac{\partial S}{\partial T}\right)_p$

6) 1-atom. plyn:
a) closed-shell – excitace $\delta\epsilon \sim 10\,eV \gg kT_{room} \simeq \frac{1}{40}\,eV$
b) hyperjemné štěpení: $s_{e^-} \cdot s_p$
$\delta\epsilon \sim 6 \cdot 10^{-6}\,eV \sim 0{,}07\,K$

c) spin-orbit interakce

Cl: $3s^2 3p^5$ $^2P \Rightarrow l = 1,\ s = 1/2 \Rightarrow$ $^2P_{3/2}$, $^2P_{1/2}$; $\delta\epsilon \sim 0{,}11\,eV \sim 1270\,K$

• další excitace mnohem výše $\Rightarrow$ 2-level systém

$$\Rightarrow C_V^{e^-} = 2\left(\frac{\delta\epsilon}{kT}\right)^2 \frac{e^{\delta\epsilon/kT}}{(2e^{\delta\epsilon/kT}+1)^2} \Rightarrow \text{Schottky}$$

7) <u>2-atom. molekula</u> – kvantově

- Molekulové vlastnosti látek (1)

- A) 1-atomový id. plyn se započtením elect. struktury
  kolik nerozmazávat - zmínit, co nepřispěje, ukázat Schottkyho

  B) 2-atom. plyn (rotace, vibrace)
  π jen kvantově, ~~případně~~ zmínit klas. limitu

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0) obecně: $\vec{q}, \vec{p}$ ... těžiště

$\vec{\varsigma}_\alpha, \vec{\pi}_\alpha$ ... vnitřní st. volnosti (jednotlivé atomy, i e^- atd.)

$$\rightarrow \mathcal{H}_1 = \frac{\vec{p}^{\,2}}{2m} + \sum_\alpha \frac{\vec{\pi}_\alpha^{\,2}}{2\mu_\alpha} + v(\vec{\varsigma}_\alpha) \rightarrow \boxed{\frac{\hat{p}^2}{2m} + \hat{h} = \hat{\mathcal{H}}_1}$$

- $\vec{p}, \vec{q}$ a $\vec{\varsigma}_\alpha, \vec{\pi}_\alpha$ nezávislé
- pohyb těžiště obv. klasický

$$\Rightarrow Z_N(\beta) = \frac{V^N}{h^{3N} N!} \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} \left[\mathrm{Tr}(e^{-\beta \hat{h}})\right]^N$$

$$\boxed{Z_N(\beta) = \frac{1}{N!} \left[V \left(\frac{2\pi m}{\beta h^2}\right)^{\frac{3}{2}}\right]^N \zeta(\beta)^N}$$

vnitřní part. funkce (zeta)

$$\zeta(\beta) = \sum_q e^{-\beta \varepsilon_q} \qquad Z_G = \sum_N Z_N e^{\beta\mu N} = \exp\left[Z_1 e^{\beta\mu}\right]$$

$$\boxed{\Omega(T,V,\mu) = -kT \log Z_G = -kTV \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \zeta(\beta)\, e^{\frac{\mu}{kT}}}$$

NB: hustota n, teplota T, hmotnost m + $k, \hbar$

klasická limita: $n \underbrace{\left(\frac{\hbar^2}{m k_B T}\right)^{3/2}}_{\text{bezrozměrná vel}} \ll 1$

$[\hbar] = \mathrm{Js}$ (*)

$[k_B T] = \mathrm{J}$

$[n] = \frac{1}{m^3}$

$\lambda = \frac{h}{p} \Rightarrow V \gg N V_{1č} \Leftrightarrow n V_{1č} \ll 1 \Leftrightarrow$

$\lambda_{therm} = \frac{h}{\sqrt{2\pi m k_B T}}$

(de Broglieho vln. délka je menší než vzdál. částic)

(takové id. plyn $\Leftrightarrow$ limita neint. kvant. plynu za podm. (*))

(7)

- **stavová rovnice** — Cv 1 ⟺ ukažte $pV = NkT$

$$p = -\frac{\partial \Omega}{\partial V} = -\frac{\Omega}{V}$$

$$n = \frac{N}{V} = -\frac{1}{V}\frac{\partial \Omega}{\partial \mu} = -\frac{\Omega}{kTV}$$

$$\frac{N}{V} = \frac{p}{kT} \Rightarrow \boxed{pV = NkT}$$

- **tepelné kapacity, vnitřní energie**

$$S = -\frac{\partial \Omega}{\partial T} = -\frac{5\Omega}{2T} + \frac{\mu \Omega}{kT^2} - \Omega \frac{d}{dT}\ln\zeta$$

$$= \left| -\Omega \overset{=pV}{=} NkT \right|$$

~~$S(T,V,\mu) = S(T,V,N(T,V,\mu))$~~ !

$$\boxed{S = \frac{5}{2}Nk - \frac{N\mu}{T} + NkT\frac{d}{dT}\ln\zeta}$$

$$U = \Omega + ST + \mu N = -NkT + \frac{5}{2}NkT - N\mu + NkT^2\frac{d}{dT}\ln\zeta + \mu N$$

$$U = \boxed{\frac{3}{2}NkT + NkT^2\frac{d}{dT}\ln\zeta(T) = U(\underline{T})}$$

Cv. 2 - najděte $U = U(T)$

$$\Rightarrow C_V = \frac{3}{2}Nk + 2NkT\frac{d}{dT}\ln\zeta(T) + NkT^2\frac{d^2}{dT^2}\ln\zeta$$

$$\left(C_V = \frac{3}{2}Nk + Nk\frac{d}{dT}\left(T^2\frac{d}{dT}\ln\zeta\right) \right)$$

Lépe z entropie - ofoč

$$C_P: \quad U(S,V,N) \to H = U + pV = U - \Omega = U + NkT$$

ano,

$$\Rightarrow \boxed{C_P = \frac{5}{2}Nk + \dots(\zeta)}$$

$$\Rightarrow \boxed{C_P - C_V = Nk}$$

~~$\left[\frac{d}{dT}\left(T^2\frac{d}{dT}\log\zeta\right) = T\frac{d^2}{dT^2}(T\log\zeta)\right]$~~

ale ano

$$\boxed{\frac{d}{dT}\left(T^2\frac{d}{dT}\,\cdot\,\right) = T\frac{d^2}{dT^2}(T\,\cdot\,)}$$

• chem. potenciál

$$= \frac{N}{V}$$

$$e^{\mu/kT} = -\frac{\Omega}{kTV}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\frac{1}{\xi(T)}$$

$$\Rightarrow \frac{\mu}{kT} = \underbrace{\ln\frac{N}{V}}_{f(p,V,T)} \underbrace{-\frac{3}{2}\ln\frac{2\pi mkT}{h^2} - \ln\xi(T)}_{f(T)}$$

$T = \text{konst} \Rightarrow \propto \ln \Leftrightarrow \propto \ln p$ (cf. id. plyn !)

• $\mu \nearrow \Leftrightarrow$ plyn se snáze zbavuje molekul

$$\Rightarrow \frac{S}{Nk} = \frac{5}{2} - \ln\frac{N}{V} + \frac{3}{2}\ln\frac{2\pi mkT}{h^2} + \ln\xi + T\frac{d}{dT}\ln\xi$$

$$\boxed{\frac{S}{Nk} = \frac{5}{2} + \frac{3}{2}\ln\frac{2\pi mkTV^{2/3}}{N^{2/3}h^2} + \frac{d}{dT}\left(T\ln\xi\right)}$$

$\Rightarrow C_V = \frac{3}{2}NkT$

$pV = NkT$

$\Rightarrow V^{2/3} = \left(\frac{Nk}{p}\right)^{2/3} T^{2/3}$

$\Rightarrow C_p = \frac{5}{2}NkT$ ✓

A) 1-atomový plyn (closed-shell ⇒ vzácné plyny)

ϵ_q ... energetické hladiny e^- obalu

• excit. energie $\sim 10\,\text{eV}$ (20 eV pro He)

• $kT \simeq \frac{1}{40}\,\text{eV}$ ... pokojová teplota (11604 K/eV) $= \frac{1}{k_B}$

$k_B = 8{,}6 \cdot 10^{-5}\,\text{eV/K}$

• degenerace zákl. stavu: $g = 2s_n + 1$ ... spin jádra

$$\Rightarrow \xi = g e^{-\epsilon_0/kT} + \sum_{q=1}^{\infty} e^{-\epsilon_q/kT} = e^{-\epsilon_0/kT}\left(g + \sum_q{}' e^{-(\epsilon_q-\epsilon_0)/kT}\right)$$

$$\Rightarrow \ln\xi = -\frac{\epsilon_0}{kT} + \ln\left[g + \sum_q{}' e^{-(\epsilon_q-\epsilon_0)/kT}\right]$$

$$(\epsilon_q - \epsilon_0)/k \sim 2\cdot 10^5\,\text{K} \Rightarrow \boxed{\ln\xi = -\frac{\epsilon_0}{kT} + \ln g}$$

⇒ žádné TD důsledky ($T\ln\xi = -\frac{\epsilon_0}{k} + T\ln g$), jen posun v U, S

b, **areaktivní jednoatom. plyny:** (Na) $\epsilon_1 - \epsilon_0 \sim 2.1\,eV$ (Na) $\hat{=}\ 24000K$

i, $g = (2s_n + 1)g_e$, g_e ... degenerace zákl. e^- stavu (typ. $s_e = 1/2$)

ii, hyperjemná struktura – interakce p a e^- spinu

$\Rightarrow$ nedeg. zákl. stav $\cancel{\epsilon_0}$, $g \to \epsilon_0, (\epsilon_0 + \delta\epsilon) \times 3$

$$\delta\epsilon = 6 \cdot 10^{-6}\,eV \sim 0{,}07\,K$$

Na = [Ne]3s
jádro spin $\frac{1}{2}$, e^- spin $\frac{1}{2}$ $\Rightarrow$ singlet + 3x triplet

$$\Rightarrow \zeta = e^{-\frac{\epsilon_0}{kT}}\left(1 + 3e^{-\delta\epsilon/kT}\right) = /kT \gg \delta\epsilon\,!/$$

$$\boxed{\zeta \doteq 4e^{-\epsilon_0/kT}} \Rightarrow \text{jako 4x deg. zákl. stav, nic TD zajímavého}$$

iii, spin-orbit interakce – jemné štěpení

Cl:	GS	$^2P_{3/2}$	$(g=4)$
[Ne]3s² (...3p5)	1. ES	$^2P_{1/2}$	$(g=2)$

$\delta\epsilon = 0{,}11\,eV \sim 1270\,K$

$$\Rightarrow \ln\zeta = -\frac{\epsilon_0}{kT} + \ln\left[4 + 2e^{-\delta\epsilon/kT}\right] \qquad x = \frac{\delta\epsilon}{kT}$$

$$= -\frac{\epsilon_0}{kT} + \ln\left[4 + 2e^{-x}\right] \qquad \frac{dx}{dT} = -\frac{x}{T}$$

Příspěvek k C_V $\quad Nk\frac{d}{dT}\left(T^2\frac{d}{dT}\ln\zeta\right)$

$$\frac{d}{dT}\ln\zeta = +\frac{\epsilon_0}{kT^2} + \cancel{\frac{4+2e^{-x}}{4+2}} \quad \frac{2\frac{x}{T}e^{-x}}{4+2e^{-x}}$$

$$T^2\ln\zeta = \frac{\epsilon_0}{k} + \frac{\frac{2\delta\epsilon}{k}e^{-x}}{4+2e^{-x}} = \frac{\epsilon_0}{k} + \frac{\delta\epsilon}{k}\frac{1}{2e^x + 1}$$

$$\frac{d}{dT} = \cancel{\frac{2\delta\epsilon}{k}\cdot\frac{x}{T}e^{-x}\frac{1}{4+2e^{-x}}} \quad \frac{\delta\epsilon}{k}\frac{+2e^x\frac{x}{T}}{(2e^x+1)^2} = \cancel{2\left(\frac{\delta\epsilon}{kT}\right)^2\frac{1}{2+e^{\delta\epsilon/kT}}}$$

$$\boxed{C_V^{e^-} = 2\left(\frac{\delta\epsilon}{kT}\right)^2\frac{e^{\delta\epsilon/kT}}{(2e^{\delta\epsilon/kT}+1)^2}} \leftarrow \text{toto je dobře!}$$

↓ OTOČ

B) Víceatom. plyny

$\hat{H} = \frac{P^2}{2m} + \hat{h}$ ← pohyb hm. středu

- ~~[illegible]~~ potřebujeme znát spektrum ϵ_q až do cca $kT \Rightarrow$ ~~Z~~ $\zeta(T)$

$\Rightarrow$ Born – Oppenheimer $|\Psi\rangle = |\Psi_n\rangle|\Psi_e\rangle$

$\Rightarrow \hat{h} = \hat{T}_n + \hat{T}_e + \hat{V}$ & $(\hat{T}_e + \hat{V})|\Psi_e\rangle = W(R_n)|\Psi_e\rangle$

- elektronové hladiny: ~~[illegible]~~ $\Delta\epsilon \sim$ eV $\sim 10^4$ K

$\Rightarrow$ pouze nejnižší stav relevantní (pro closed-shell molekuly?

(neplatí pro pevné látky!)

$\boxed{CO: \Delta\epsilon \sim 8{,}2\,eV}$ ADC(2)x

$\boxed{HCl: \Delta\epsilon \sim 7{,}8\,eV}$ cc-pVDZ

$\Rightarrow (\hat{T}_n + \hat{W})|\Psi_n\rangle = \epsilon|\Psi_n\rangle$

$\hat{T}_n = \sum_i \frac{\pi_i^2}{2\mu_i}$ – ~~[illegible]~~ pohyb hm. středu je odsep.

$\Rightarrow \boxed{\hat{h} = \frac{\hat{\pi}^2}{2\mu} + W(\hat{\rho})}$ pro dvouatom. molek.

"centrální pole

přeskoč na 7

$\epsilon_q = \epsilon_{nlm}$

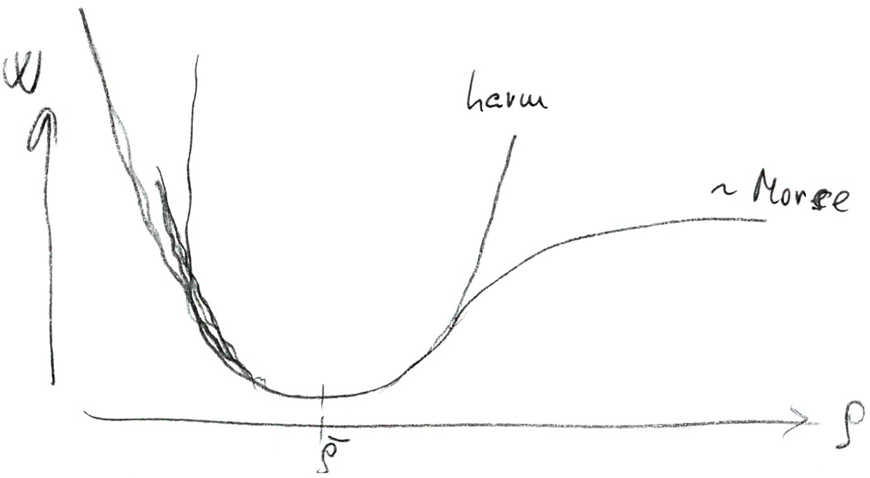
$l \to 2l+1$ ~~rot. hl.~~ deg., rotační hladiny

$n \to$ vib. hladiny

spin $\to$ pouze další degenerace $(\hat{h} \neq \hat{h}(\sigma))$

HCl: $\Theta_r = 15\,K = 1{,}3 \cdot 10^{-3}\,eV$

$\Theta_v = 4100\,K = 0{,}35\,eV$ $\quad \propto \frac{1}{\sqrt{\mu}}$



⇓ pro těžší atomy vib. relevantní i při nižší teplotách

Klasický přístup: ρ se málo liší od $\bar\rho$

$$W(\rho) \approx W_0 + \frac{1}{2}\mu\omega^2(\rho-\bar\rho)^2$$

$$\xi_{cl}(T) = \frac{1}{h^3}\int d^3\pi\, d\varphi\, d\vartheta\, \underset{d\rho}{\rho^2 \sin\vartheta}\, e^{-\beta\left(\frac{\pi^2}{2\mu} + W_0 + \frac{1}{2}\mu\omega^2(\rho-\bar\rho)^2\right)}$$

$$= \frac{4\pi}{h^3} e^{-\beta \overset{=W_0}{\epsilon_0}} \bar\rho^2 \int d^3\pi\, d\rho\, e^{-\beta\left(\frac{\pi^2}{2\mu} + \frac{1}{2}\mu\omega^2(\rho-\bar\rho)^2\right)}$$

$$= \frac{4\pi}{h^3} e^{-\beta\epsilon_0}\bar\rho^2 \sqrt{\frac{2\pi\mu}{\beta}}^3 \sqrt{\frac{2\pi}{\beta\mu\omega^2}} =$$

$$= e^{-\beta\epsilon_0}\bar\rho^2 \frac{2\cancel{(2\pi)^3}}{\hbar^3\beta^2}\frac{\mu}{\omega} = \boxed{e^{-\beta\epsilon_0}\frac{T}{\Theta_r}\frac{T}{\Theta_v} = \xi_{cl}(T)}$$

$$\boxed{\Theta_v = \frac{\hbar\omega}{k} \qquad \Theta_r = \frac{\hbar^2}{2\mu\bar\rho^2 k} \qquad \Theta_r \ll \Theta_v \ll T}$$

- jen tak platí klas. approx – rot. i vib. hladiny ~~kvazi~~ ef. kontinuum
- nesmíme se však příliš vzdálit od $\bar\rho$

$$\boxed{C_V^{vibrot} = NkT\frac{d^2}{dT^2}\left(T\frac{d}{dT}\log\xi\right) = 2Nk}$$ cf ~~eq~~ ekvipart. teorém ($\frac{1}{2}k$ pro kaqd. st. volnosti)

$$\log\xi = -\frac{\epsilon_0}{kT} + 2\log T \xrightarrow{d_T} \frac{\epsilon_0}{kT^2} + \frac{2}{T} \xrightarrow{T^2} \frac{\epsilon_0}{k} + 2T$$

celkem $C_V = \frac{7}{2}Nk$ (1 vib $(p^2 + \rho^2)$ + 2 úhly)

Typické molekuly: $\Theta_v^{at}{}_{room} \ll \Theta_{rot} \Rightarrow C_V = \frac{5}{2}Nk$

($\Rightarrow$ pouze $\underbrace{\varphi, \vartheta}_{0}$, $\underbrace{p_\varphi, p_\vartheta}_{kT}$ jsou nezamrzlé st. volnosti)

$\Rightarrow$ tuhý rotátor

Víceatom: (Troom)
- vib. zamrzlé
- rot. – 3 eulerovy úhly $\Rightarrow$ 3 sdruž. hybnosti $\Rightarrow C^{rot} = \frac{3}{2}Nk \Rightarrow C_V = 3Nk$

Kvantové (dvouatom. plyn) (7)

- zaned. (mag.) spin-spin interakci e a jader
- Pauli ⇒ $|\Psi_e\rangle$ antisym. vůči záměně e^-
- $|\Psi_n\rangle$ – sym. antisym. vůči záměně pro boson. jádra / fermion. } pro ident. atomy (DÚ)

- různé atomy: HCl, rozvoj do parc. vln $\psi = R(\rho)\,Y_{lm}(\vartheta,\varphi)$

$$\left[-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{d\rho^2}+\frac{2}{\rho}\frac{d}{d\rho}-\frac{l(l+1)}{\rho^2}\right)+\mathcal{W}(\rho)\right]R_{nl}(\rho)=\epsilon_{nl}R_{nl}(\rho)$$

hladiny $(2l+1)$-deg. $\qquad R=\frac{\phi}{\rho}$

$$\rho\simeq\bar\rho \Rightarrow \frac{\hbar^2 l(l+1)}{2\mu\rho^2}\to\frac{\hbar^2 l(l+1)}{2I}\quad;\quad \phi=\rho R(\rho)$$

$x=\rho-\bar\rho$ $\boxed{\text{harmonická approx.}}$ $\qquad x=\rho-\bar\rho$

$$\Rightarrow\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}+\frac{1}{2}\mu\omega^2x^2\right]\phi_{ln}(x)=\left(\epsilon_{ln}-\mathcal{W}_0-\frac{\hbar^2 l(l+1)}{2I}\right)\phi_{ln}(x)$$

$$\Rightarrow\boxed{\epsilon_{ln}=\epsilon_0+l(l+1)k\Theta_r+nk\Theta_v}\qquad \epsilon_0=\mathcal{W}_0+\frac{1}{2}\hbar\omega$$

$$\Theta_r=\frac{\hbar^2}{2Ik}\qquad \Theta_v=\frac{\hbar\omega}{k}$$

$$\Rightarrow\boxed{\zeta(T)=g\,\zeta_r(T)\,\zeta_v(T)\,e^{-\epsilon_0/kT}}$$

$$g=(2s_n+1)(2s_e+1)g_e$$

g_e: deg. e^- stavu (nespinová)

$$\zeta_r(T)=\sum_{l=0}^{\infty}(2l+1)e^{-l(l+1)\Theta_r/T}$$

$$\zeta_v(T)=\sum_{n=0}^{\infty}e^{-n\frac{\Theta_v}{T}}=\frac{1}{1-e^{-\Theta_v/T}}\Rightarrow C^{vib}=Nk\left[\frac{\Theta_v/2T}{\sinh(\Theta_v/2T)}\right]^2$$

toto je klas. limita; musí ale být $k_BT\ll E_{diss}$

Spec.:
- $\Theta_v\gg T\Rightarrow\zeta_v=1$ $\qquad$ Typ. (HCl): $\Theta_r=15\,K \Leftrightarrow 1{,}3\cdot10^{-3}\,eV$, $\Theta_v=0{,}35\,eV\Leftrightarrow 4\,100\,K$
- $C_V^r=Nk$: $\boxed{\Theta_r\ll T}\Rightarrow\zeta_r$ nahradím integrálem $\to\frac{T}{\Theta_r}=\zeta_r$ (viz DÚ)
- $C_V^v=Nk$: $\boxed{\Theta_v\ll T}\Rightarrow\zeta_v=\frac{T}{\Theta_v}$

$\boxed{\text{Stejné atomy: DÚ}}$