Statistische Thermodynamik

Verteilungsfunktion MB/BE/FD

Zustandssumme

$$q = \sum g_i e^{-\beta \varepsilon_i}$$

(+QM)

q_{trans}

q_{rot}

q_{vib}

q_{el}

$\langle \varepsilon \rangle$, Übergang MB→FD/BE, Symmetrie

Molekulare Zustandssumme $\boldsymbol{q_{mol}}$

(+TD)

Innere Energie (U), Entropie (S) als Funktion von $\boldsymbol{q_{mol}}$

$$\langle \varepsilon \rangle = kT^2 \left(\frac{\partial ln q_{mol}}{\partial T} \right)$$

Nullpunktsentropie, innere Energie und Entropie im Gas/Kristall

Thermodynamische Funktionen: A, p, G, C_v, μ, K

Zustandssumme der Translation

$$q_{trans,3D} = \left(\sqrt{\frac{2\pi mkT}{h^2}}\right)^3 V = \frac{V}{\Lambda^3}$$

$$q_{trans,3D}(O_2, V = 1l, T = 298K) = 1.8 \cdot 10^{29}$$
$$N(O_2, V = 1l, T = 298K) = 2.7 \cdot 10^{22}$$

$$\frac{N}{q} = e^{-\alpha} = 1.5 \cdot 10^{-7} \ll 1$$

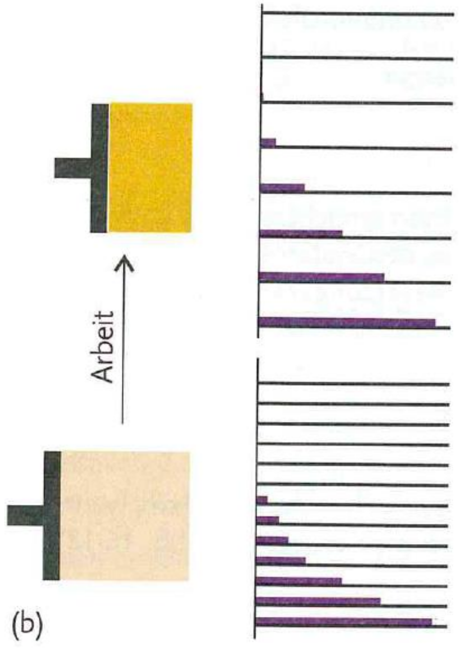

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Tabelle 3.1.

Stoff	T/K	$\frac{N}{q_{trans}}$
Helium (l)	4	2,2
Helium (g)	4	0,15
Helium (g)	20	0,0028
Helium (g)	100	$4{,}8 \cdot 10^{-5}$
Neon (l)	27	0,015
Neon (g)	27	$1{,}1 \cdot 10^{-4}$
Neon (g)	100	$4{,}3 \cdot 10^{-6}$
Argon (l)	86	$7{,}0 \cdot 10^{-4}$
Argon (g)	86	$2{,}2 \cdot 10^{-6}$
Elektronen in Na-Metall	300	2025

$$\frac{N}{q_{trans}} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}$$

Fermi-Dirac-Verteilung!

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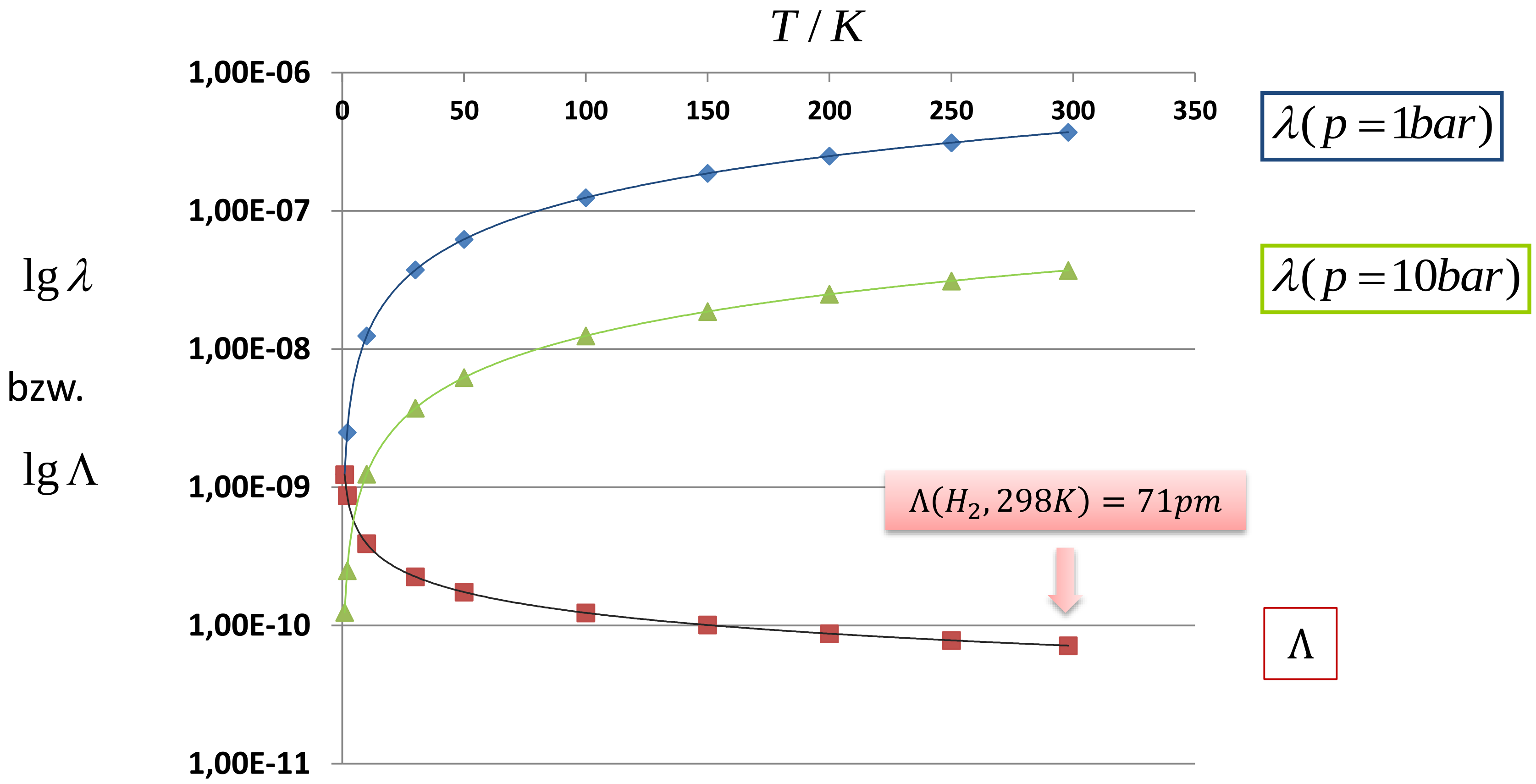
$$q_{trans,3D} = \frac{V}{\Lambda^3}$$

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}} \qquad \lambda = \frac{kT}{\sqrt{2}\sigma p}$$



Verteilungsfunktionen

Maxwell-Boltzmann
(MB)

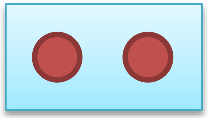
$$N_j = g_j \frac{1}{e^{\alpha} e^{\beta \varepsilon_j}}$$

$$\overline{N_j} \ll 1$$

$$\frac{N_j}{N} = \frac{g_j e^{-\beta \varepsilon_j}}{\sum g_i \, e^{-\beta \varepsilon_i}} \qquad e^{-\alpha} = \frac{N}{q}$$

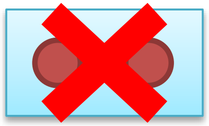
Bose-Einstein
(BE)

$$N_j = g_j \frac{1}{e^{\alpha} e^{\beta \varepsilon_j} - 1}$$



Fermi-Dirac
(FD)

$$N_j = g_j \frac{1}{e^{\alpha} e^{\beta \varepsilon_j} + 1}$$



$$N_{j,FD} < N_{j,MB} < N_{j,BE}$$

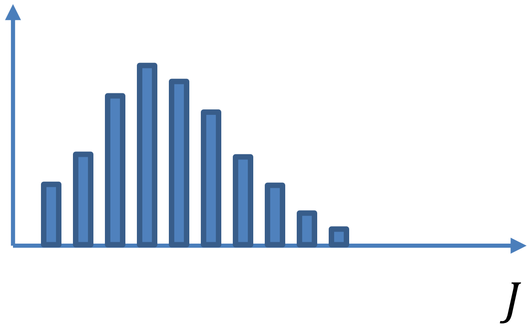
Zustandssumme der Rotation

$$q_{rot} = \sum_{J=0} (2J+1) exp\left(-J(J+1)\frac{hcB}{kT}\right)$$

$$\theta_{rot} = \frac{hcB}{k} = \frac{\hbar^2}{2kI}$$

$$n_0 = 1, n_1 = 3exp\left(-2\frac{\theta}{T}\right),$$

$$n_2 = 5exp\left(-6\frac{\theta}{T}\right) \dots$$



$T >> \theta_{rot}$: $$q_{rot} = \frac{T}{\sigma\theta_{rot}}$$

Symmetriezahl

Charakteristische Rotationstemperatur

Tabelle 5.1. Rotations- und Schwingungskonstanten und chemische Dissoziationsenergie zweiatomiger Moleküle[a])

Molekül	μ / amu	r_e / pm	θ_r / K	σ	θ_v / K	D_0 / eV
$^{1}H_2$	0,50391	74,12	85,36	2	6244	4,4773
$^{1}H^{2}H$ (HD)	0,67171	74,12	64,26	1	5420	4,5128
$^{2}H_2$ (D_2)	1,00705	74,12	43,04	2	4440	4,5553
$^{14}N_2$	7,00154	109,4	2,863	2	3383	9,760
$^{12}C^{16}O$	6,85621	112,83	2,766	1	3112	11,09
$^{14}N^{16}O$	7,46676	115,08	2,440	1	2729	6,50
$^{16}O_2$	7,99745	120,75	2,068	2	2265	5,116
$^{19}F_2$	9,49910	140,9	1,270	2	1312	1,604
$^{35}Cl_2$	17,4822	198,78	0,3501	2	803	2,484
$^{79}Br^{81}Br$	39,9524	228,09	0,1165	1	464	1,971
$^{127}J_2$	63,4502	266,66	0,0537	2	308	1,544
$^{1}H^{7}Li$	0,88123	159,54	10,66	1	2006	2,429
$^{1}H^{16}O$	0,94808	97,08	26,64	1	5315	4,392
$^{1}H^{19}F$	0,95705	91,68	60,875	1	5890	5,86
$^{1}H^{35}Cl$	0,97959	127,46	15,021	1	4265	4,436
$^{1}H^{81}Br$	0,99511	141,45	12,012	1	3779	3,755
$^{1}H^{127}J$	0,99988	160,90	9,246	1	3293	3,053
$^{7}Li_2$	3,50800	267,25	0,963	2	504	1,12
$^{23}Na_2$	11,4949	307,86	0,222	2	229	0,75
$^{39}K_2$	19,48185	392,3	0,0807	2	133	0,51
$^{23}Na^{35}Cl$	13,8707	236,06	0,313	1	525	4,25
$^{39}K^{79}Br$	26,0850	282,07	0,117	1	306	3,925

$$\theta_{rot} = \frac{hcB}{k} = \frac{\hbar^2}{2kI}$$

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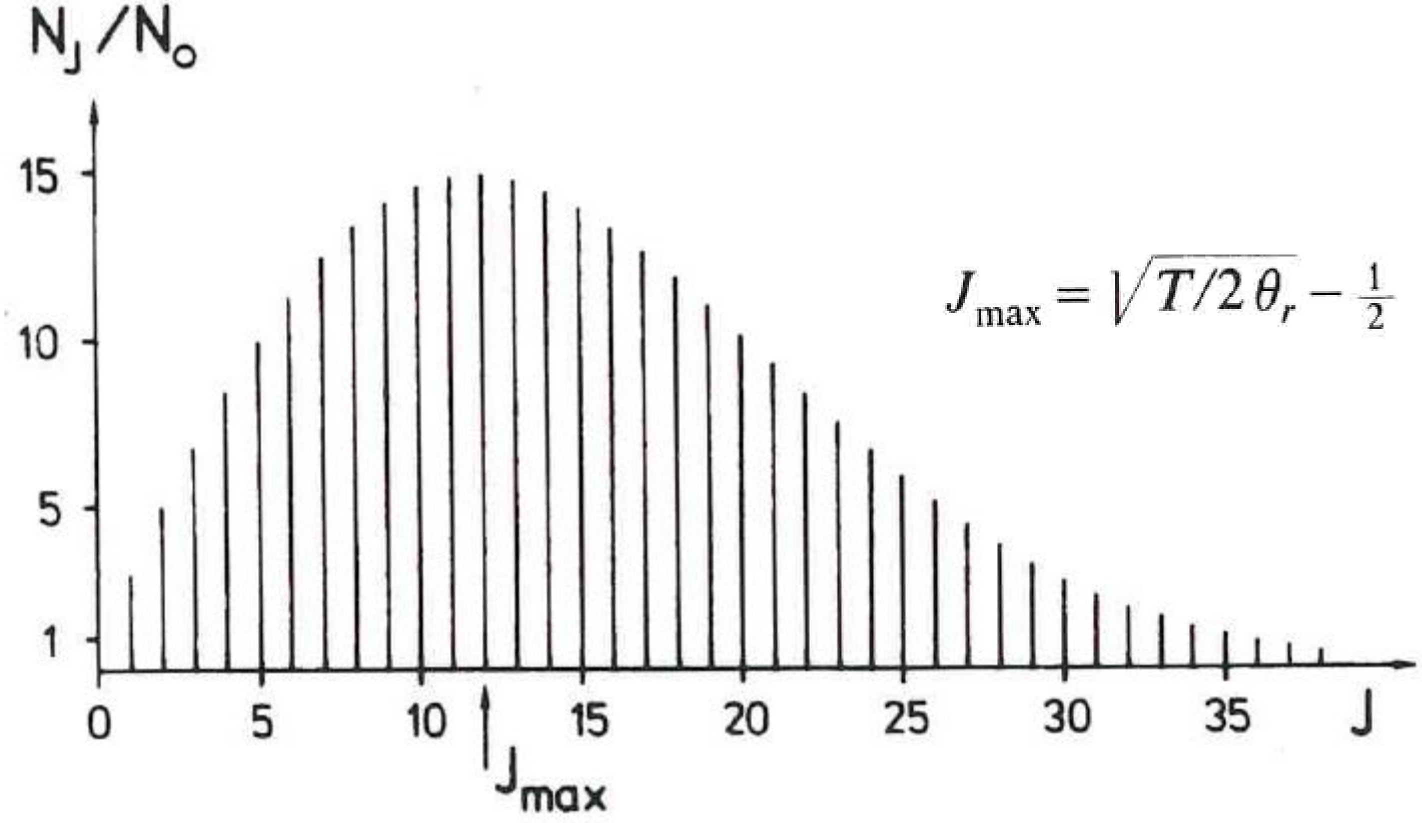
Besetzungszahlen der Rotation



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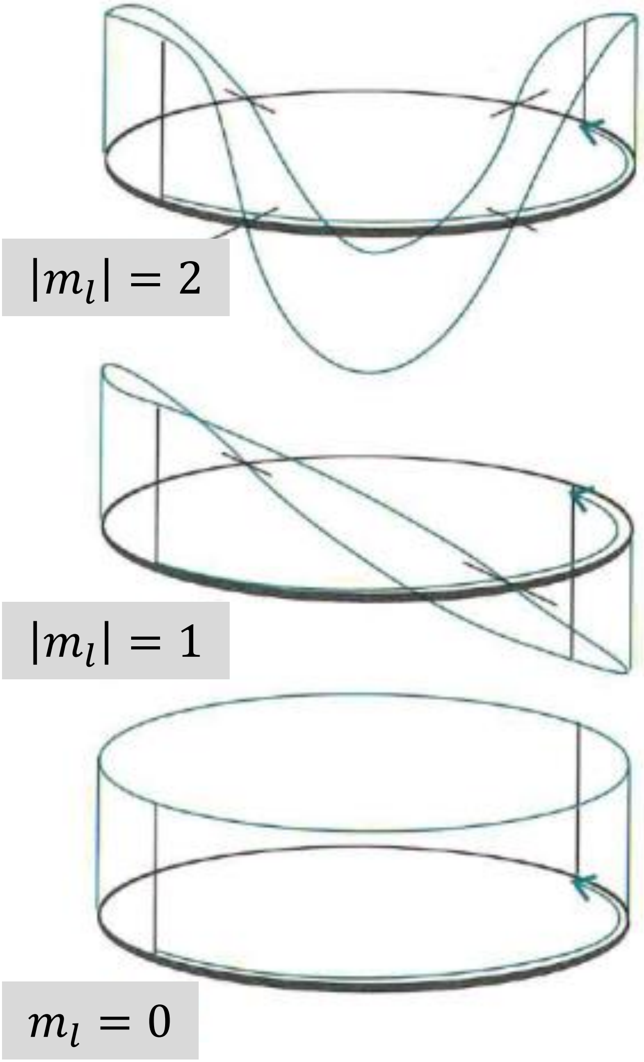
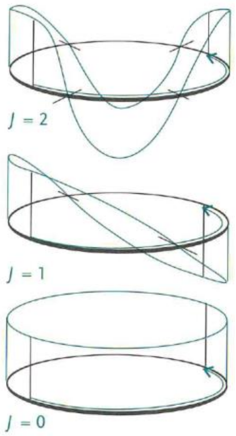
Wellenfunktionen der Rotation

$$\psi_{m_l}(\phi) = e^{im_l\phi}\frac{1}{\sqrt{2\pi}}$$

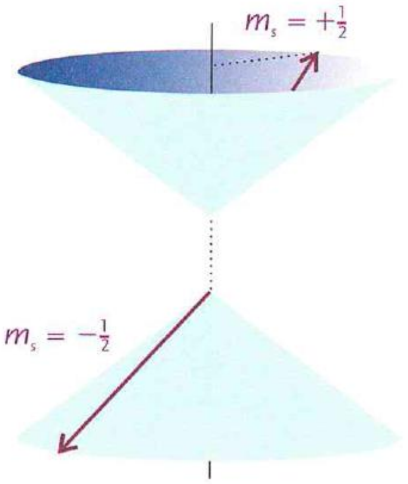
$$e^{im_l\phi} = cos(m_l\phi) + isin\,(m_l\phi)$$



Rotationszustandssumme von Wasserstoff



Pauli-Prinzip: beim Austausch zweier Fermionen muss sich das Vorzeichen der Gesamtwellen-funktion ändern.

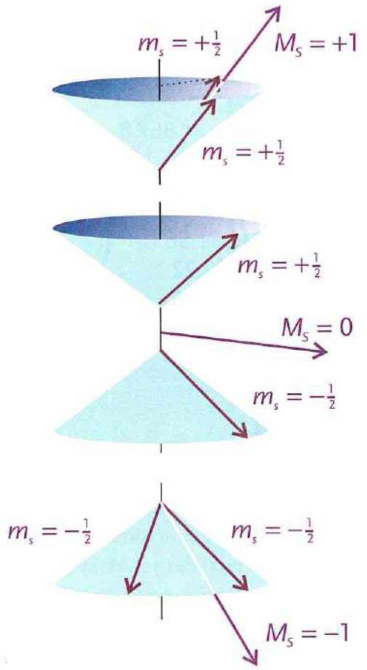


25%

para-H_2

↑↓

J gerade



75%

ortho-H_2

↑↑

J ungerade

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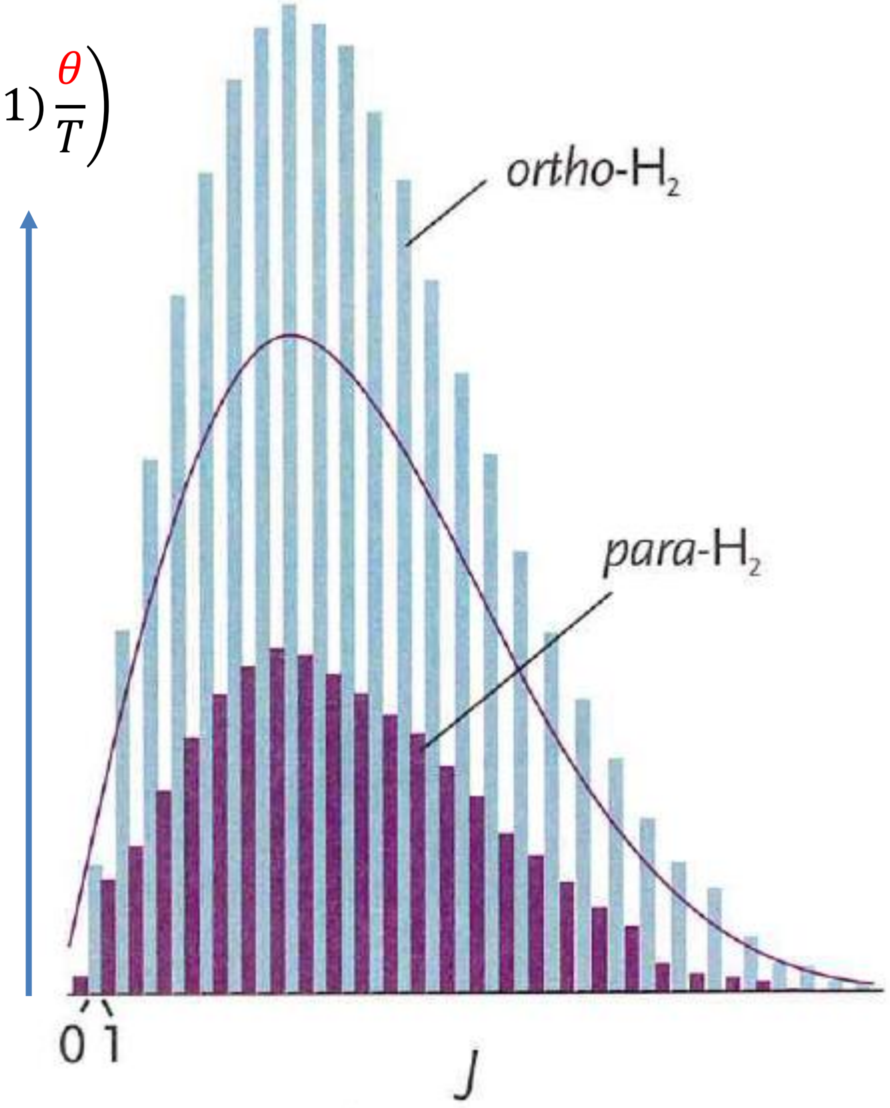
Rotationszustandssumme von Wasserstoff

$$q_J = (2J+1)exp\left(-J(J+1)\frac{\theta}{T}\right)$$



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Die molekulare Zustandssumme

$$q_{mol} = q_{el}\left(\frac{V}{\left(\frac{h}{\sqrt{2\pi m k T}}\right)^{3}}\right)\left(\frac{T}{\sigma\theta_{rot}}\right)\left(\frac{1}{1-e^{-\frac{\theta_{vib}}{T}}}\right)$$

g_0

$$\theta_{rot} = \frac{hcB}{k} = \frac{\hbar^2}{2kI}$$

$$\theta_{vib} = \frac{hc\tilde{\nu}}{k} = \frac{\hbar}{k}\sqrt{\frac{\tilde{k}}{\mu}}$$