1

1.1

$$
\begin{aligned}
\hat{H}\psi &= \sum_n \hat{H}_n \prod_m \psi_m \\
&= \sum_n \hat{E}_n \prod_m \psi_m \\
&= \sum_n \hat{E}_n \psi = E\psi
\end{aligned}
$$

1.2

(1.14):

$$\chi(\mathbf{R}, t) = \sum_n c_n \phi_n(\mathbf{R}) e^{-i\varepsilon_n t/\hbar}$$

(1.11):

$$i\hbar \frac{\partial \chi(\mathbf{R}, t)}{\partial t} = \left[\hat{T}_{\mathsf{nuc}} + E_i(\mathbf{R})\right] \chi(\mathbf{R}, t)$$

Substitute (1.14) into (1.11)

$$
\begin{aligned}
i\hbar \frac{\partial}{\partial t}\left(\sum_n c_n \phi_n(\mathbf{R}) e^{-i\varepsilon_n t/\hbar}\right) &= \left[\hat{T}_{\mathsf{nuc}} + E_i(\mathbf{R})\right] \sum_n c_n \phi_n(\mathbf{R}) e^{-i\varepsilon_n t/\hbar} \\
i\hbar \sum_n c_n \phi_n(\mathbf{R}) \frac{\partial e^{-i\varepsilon_n t/\hbar}}{\partial t} &= \sum_n c_n \left[\hat{T}_{\mathsf{nuc}} + E_i(\mathbf{R})\right] \phi_n(\mathbf{R}) e^{-i\varepsilon_n t/\hbar} \\
\sum_n c_n \phi_n(\mathbf{R}) \varepsilon_n e^{-i\varepsilon_n t/\hbar} &= \sum_n c_n \varepsilon_n \phi_n(\mathbf{R}) e^{-i\varepsilon_n t/\hbar}
\end{aligned}
$$

where we have used $\left[\hat{T}_{\mathsf{nuc}} + E_i(\mathbf{R})\right] \phi_n(\mathbf{R}) = \varepsilon_n \phi_n(\mathbf{R})$, since $\phi_n(\mathbf{R})$ is the stationary state of $\hat{H} = \hat{T}_{\mathsf{nuc}} + E_i(\mathbf{R})$ with eigenvalue ε_n.

Remark This is only valid for time-independent Hamiltonian.

1.3

The eigenspectrum of quantum rigid rotor:

$$E_f = \hbar^2 f(f+1)/(2I), f = 0, 1, 2, \ldots$$

where $2f + 1 = \omega_f$ The corresponding Boltzmann distribution:

$$\begin{aligned} P(f) &= \frac{\omega_f}{Q} e^{-E_f/k_B T} \\ &= \frac{(2f+1)e^{-\frac{\hbar^2}{2Ik_B T} f(f+1)}}{Q} \end{aligned}$$

where $Q = \sum_g \omega_g e^{-E_g/k_B T}$. Then,

$$\begin{aligned} \frac{\partial P(f)}{\partial f} &= \frac{1}{Q}(2f+1)e^{-\frac{\hbar^2}{2Ik_B T} f(f+1)} \\ &= \frac{1}{Q} e^{-\frac{\hbar^2}{2Ik_B T} f(f+1)} \left[2 - (2f+1)\frac{\hbar^2}{2Ik_B T}(2f+1) \right] \end{aligned}$$

Then

$$\begin{aligned} (2f_{\mathsf{max}} + 1)^2 &= \frac{4Ik_B T}{\hbar^2} \\ \Rightarrow f_{\mathsf{max}} &= \frac{\sqrt{Ik_B T}}{\hbar} - \frac{1}{2} \end{aligned}$$

1.4

The probability of finding translational energies that exceed E^*

$$\begin{aligned} P(E > E^*) &= \int_{E^*}^{+\infty} P(E) dE \\ &= \int_{E^*}^{+\infty} 2\pi \left(\frac{1}{\pi k_B T} \right)^{3/2} E^{\frac{1}{2}} e^{-\frac{1}{k_B T} E} dE \end{aligned}$$

Set $E/(k_BT) = u^2$, then $E^{1/2} = (k_BT)^{1/2}u$, $dE = k_BT2udu$,

$$
\begin{aligned}
P(E > E^*) &= \frac{2\pi}{(\pi k_BT)^{3/2}} \int_{(E^*/k_BT)^{1/2}}^{+\infty} (k_BT)^{1/2} u e^{-u^2} k_BT2udu \\
&= \frac{4}{\sqrt{\pi}} \int_{(E^*/k_BT)^{1/2}}^{+\infty} u^2 e^{-u^2} du \\
&= 1 - \mathsf{erf}(\sqrt{(E^*/k_BT)}) + \frac{2(E^*/k_BT)^{1/2}}{\sqrt{\pi}} e^{-E^*/k_BT}
\end{aligned}
$$

Subtract e^{-E^*/k_BT}.

$$
\Delta(E^*) \equiv 1 - \mathsf{erf}(\sqrt{(E^*/k_BT)}) + \left(\frac{2(E^*/k_BT)^{1/2}}{\sqrt{\pi}} - 1 \right) e^{-E^*/k_BT}
$$

When $E^* = 0$, erf$(0) = 0$, $\Delta(0) = 0$.

When $E^* = 0.5k_BT$, erf$(0.5) = 0.5205$, $\Delta(0.5) = 0.3569$.

When $E^* = k_BT$, erf$(1.0) = 0.8427$, $\Delta(1.0) = 0.2045$.

When $E^* = 2k_BT$, erf$(2.0) = 0.9953$, $\Delta(2.0) = 0.0853$.

When $E^* \gg k_BT$, erf$(\infty) = 1$, $\Delta(\infty) = \lim_{E^* \to \infty} \frac{2(E^*/k_BT)^{1/2}}{\sqrt{\pi}} e^{-E^*/k_BT} = 0$.

1.5

(a)

$$
\begin{aligned}
\langle E \rangle &= \int_0^\infty 2\pi \left(\frac{1}{\pi k_BT} \right)^{3/2} E^{3/2} \exp(-E/k_BT) dE \\
&= 2\pi \left(\frac{k_BT}{\pi k_BT} \right)^{3/2} k_BT \int_0^\infty \left(\frac{E}{k_BT} \right)^{3/2} \exp(-E/k_BT) dE/(k_BT) \\
&= 2 \left(\frac{1}{\pi} \right)^{1/2} k_BT \Gamma(\frac{5}{2}) \\
&= \frac{3}{2} k_BT
\end{aligned}
$$

(b)

$$
\begin{aligned}
\sigma_x^2 &= \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle \\
&= \langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2 \\
&= \langle x^2 \rangle - \langle x \rangle^2
\end{aligned}
$$

(c)

$$
\begin{aligned}
\sigma_E^2 &= 2\left(\frac{1}{\pi}\right)^{1/2} (k_B T)^2 \int_0^\infty \left(\frac{E}{k_B T}\right)^{5/2} \exp(-E/k_B T) dE/(k_B T) - \frac{9}{4}(k_B T)^2 \\
&= 2\left(\frac{1}{\pi}\right)^{1/2} (k_B T)^2 \Gamma(\frac{7}{2}) - \frac{9}{4}(k_B T)^2 \\
&= \frac{3}{2}(k_B T)^2
\end{aligned}
$$