# UNIVERSITY OF
# NOTRE DAME

# Physical Chemistry for Chemical Engineers (CHE 30324)

Prof. William F. Schneider

**NAME (PRINT):**_____

**NETID (PRINT):**_____

> *AS A MEMBER OF THE NOTRE DAME COMMUNITY, I WILL NOT PARTICIPATE IN OR TOLERATE ACADEMIC DISHONESTY*

**SIGNED:** _____

**WRITE YOUR SOLUTIONS IN THE SPACE INDICATED, MAKING SURE YOUR APPROACH IS CLEAR. USE THE BACK OF THE TABLES PAGES IF YOU NEED ADDITIONAL SCRATCH SPACE. WRITE YOUR NETID IN THE UPPER RIGHT OF EACH PAGE.**

# 1 Tunneling will bring us together (72 pts)

Applications of the Schrödinger equation to molecules is complicated by the many interactions between electrons and nuclei. Here we'll look at $N_2$.

$$N_A \text{——————} N_B$$
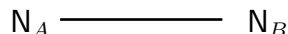
**1.1** (4 pts) How many of what types of elementary particles make up an $N_2$ molecule?

2 $N^{7+}$ nuclei

14 $e^-$

**1.2** (10 pts) What are the types of energies/interactions between those particles that contribute to the total energy of an isolated, otherwise stationary $N_2$ molecule? Be concise but complete.

| Type | Particles |
|---|---|
| Coulomb | N nucleus – N nucleus |
| " | N nucleus – electron |
| " | electron – electron |
| Kinetic | N nuclei |
| " | electrons |
| | |
| | |
| | |

1.3 (4 pts) In solving the Schrödinger equation for $N_2$, we commonly make the "Born-Oppenheimer," or clamped nucleus, approximation. What is that approximation. Relate to the table above if possible.

*Take nuclei as stationary. Neglect nuclear kinetic energy.*

1.4 (12 pts) The standard strategy for computing the $N_2$ energy is "density functional theory," where we write an equation for the electron wavefunctions as below. **Briefly identify the meaning of each term as well as the sign (positive or negative) of the contribution to the $N_2$ energy.**

$$\left\{ -\frac{\hbar^2}{2m_e}\nabla^2 + \hat{v}_{Ne} + \hat{v}_{ee}[\rho] \right\} \psi_i = \epsilon_i \psi_i$$

1. $-\frac{\hbar^2}{2m_e}\nabla^2$:

   *electron kinetic energy*
   *positive*

2. $\hat{v}_{Ne}$:

   *nuclear - electron attraction*
   *negative*

3. $\hat{v}_{ee}[\rho]$:

   *electron - electron repulsion*
   *positive*

1.5 (4 pts) Briefly, what is the relationship between $\rho$ and the $\psi_i$ in the equation above. Either an equation or words is acceptable.

*$\psi_i$ individual electron wavefunctions*

*$\rho$ total electron density*

$$\rho = \sum_i |\psi_i|^2$$

1.6    (4 pts) Briefly, what does it mean for the equation above to be solved "self-consistently"?

$v_e[\rho]$ depends on unknown $\rho$.
Guess $\rho$, solve for $\psi_i$, check, repeat
until $\rho$ in $+$ $\psi_i$ out are consistent.

1.7    (12 pts) Solving the equation (plus the analogous equation for an N atom) yields the
       wavefunction energies sketched below. Complete the diagram by adding in the elec-
       trons, paying attention to all the rules for doing so, and drawing appropriate lines
       between atomic and molecular energy states.
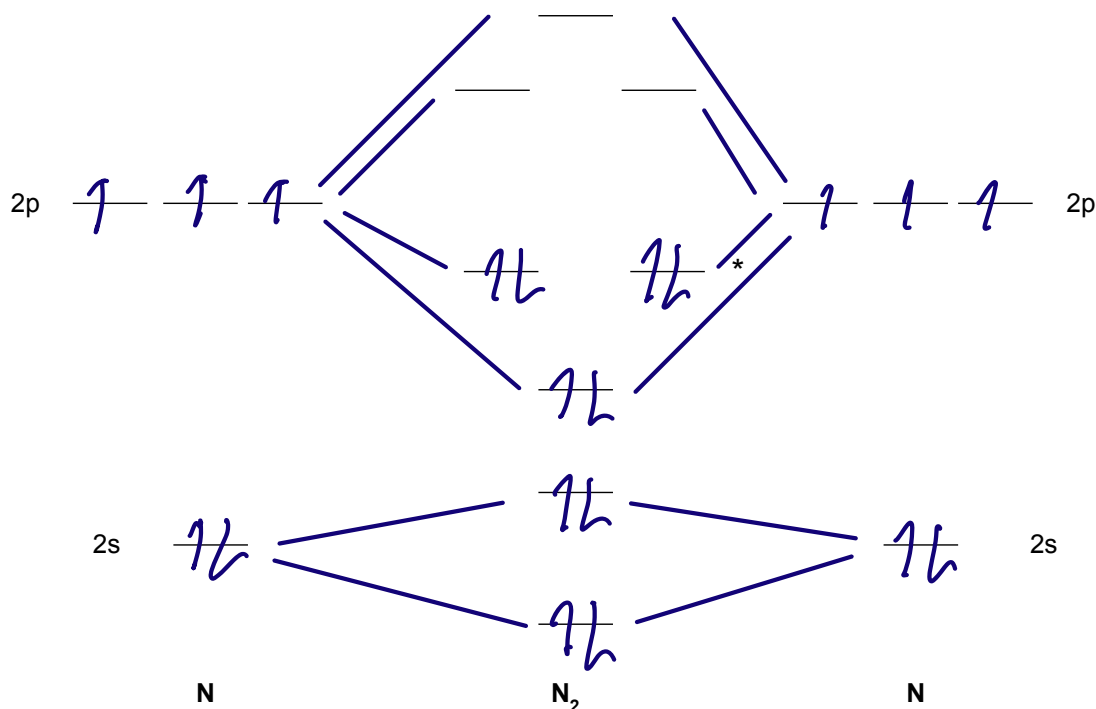


1.8    (2 pts) Based on your diagram, what is the bond order of $N_2$?

$$\frac{8 \text{ bonding} - 2 \text{ antibonding}}{2} = 3$$

1.9   (4 pts) On the graph below, sketch approximately the molecular wavefunction indicated by a star in the diagram above.
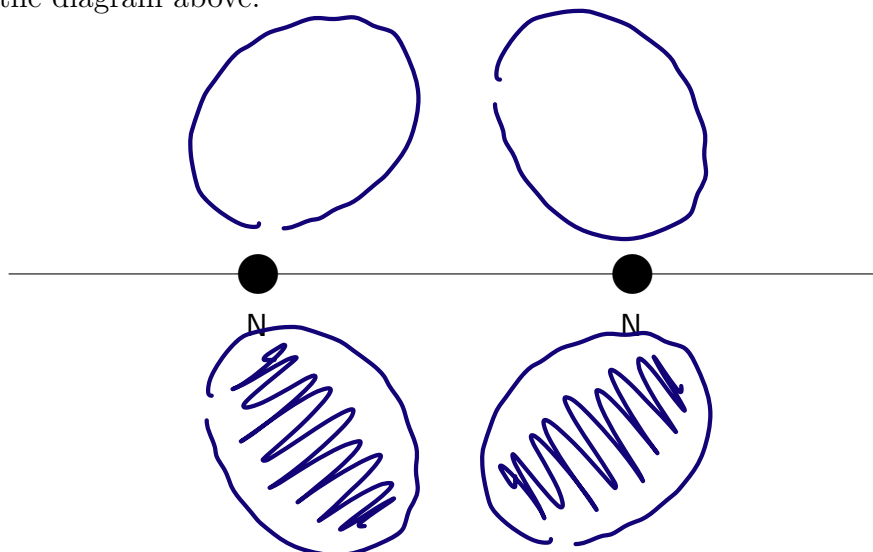


1.10   (4 pts) On the graph below, sketch the value of the overlap integral $S$ vs interatomic distance $R$ for the wavefunction indicated by a star. Remember to label each axis with appropriate units.
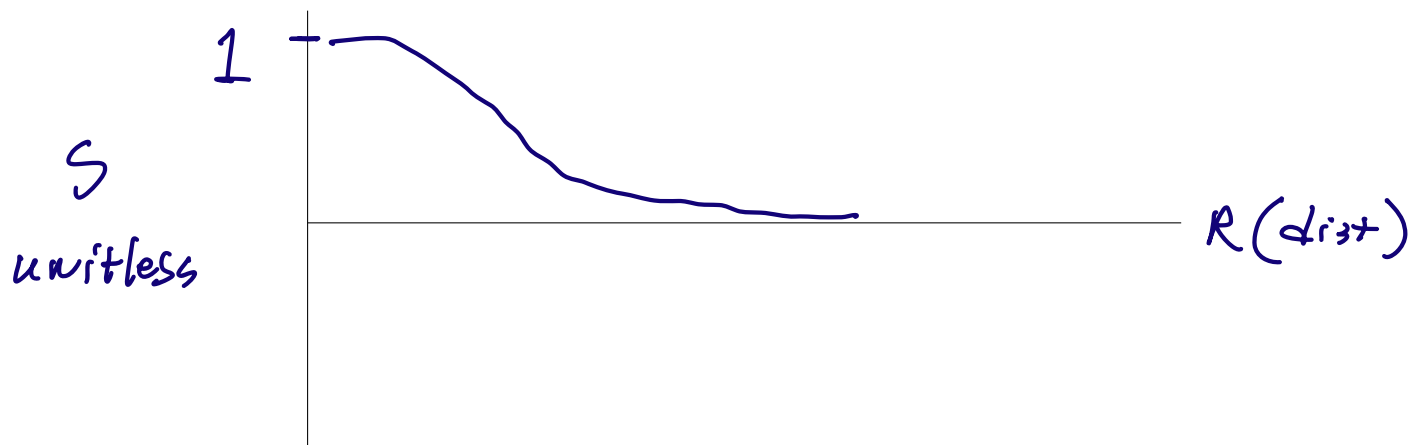
1.11 (8 pts) On the graph below, approximately sketch the $N_2$ total energy vs interatomic distance. Indicate on the graph the equilibrium internuclear distance ($R_e$) and the bond dissociation energy. Remember to properly label both axes, including appropriate units.

energy

$R_e$

R

BDE

(could remove ZPE)
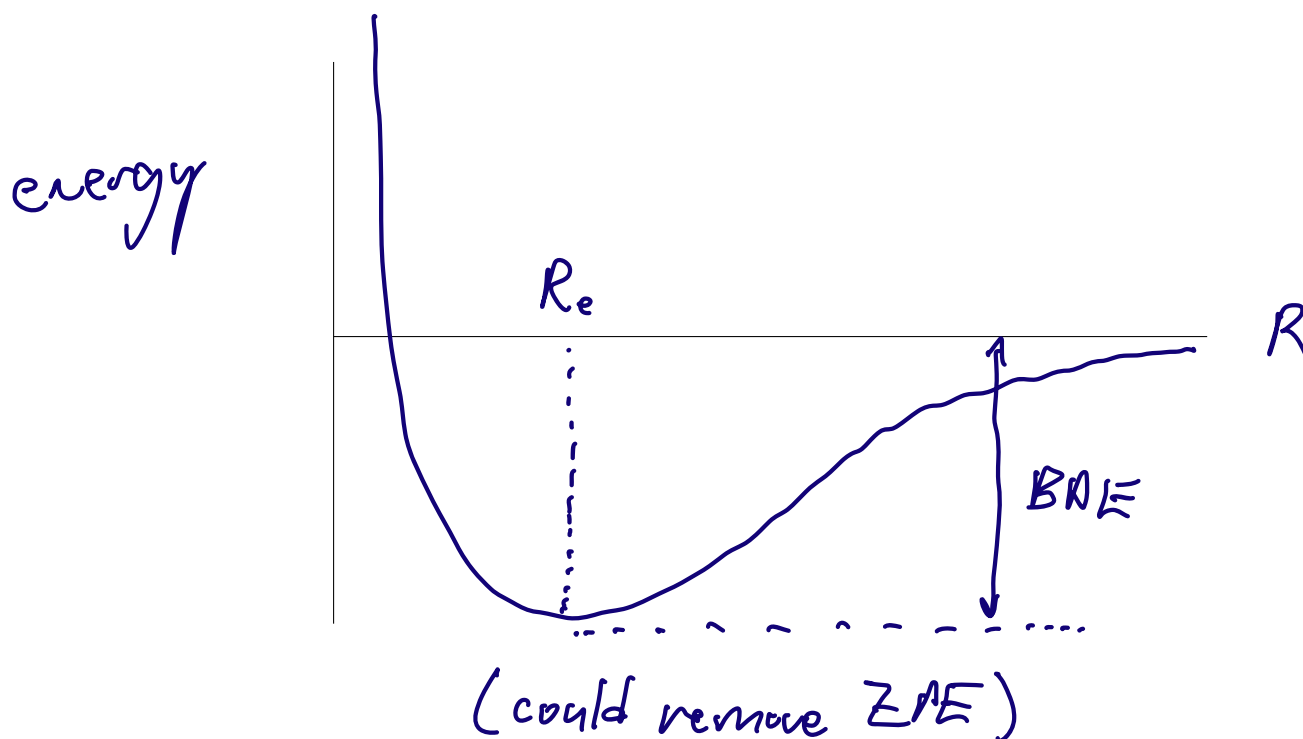
1.12 (4 pts) O is one atom to the right of N in the periodic table. How do you expect the equilibrium bond distance ($R_e$) and and the bond dissociation energy of $O_2$ to compare to that of $N_2$? (It might help to refer back to your molecular wavefunction energy diagram!)

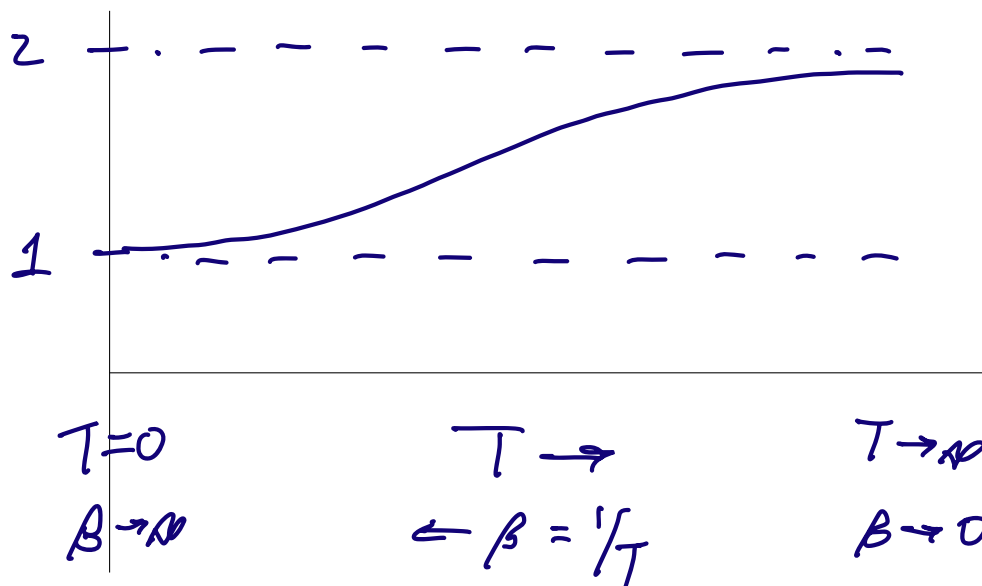2 more antibonding $e^-$

$R_e$ ↑

$|BDE|$ ↓

## 2   Energy, entropy, temperature (28 pts)

Consider a box that contains $N$ distinguishable marbles, each of which can exist in one of two energy states, 0 or $\varepsilon$.

**2.1**   (4 pts) Imagine this box is put into thermal equilibrium with some large reservoir at temperature $T$. Write down the partition function $q(\beta)$ for *one marble* in the box, as a function of $\beta = 1/k_B T$.

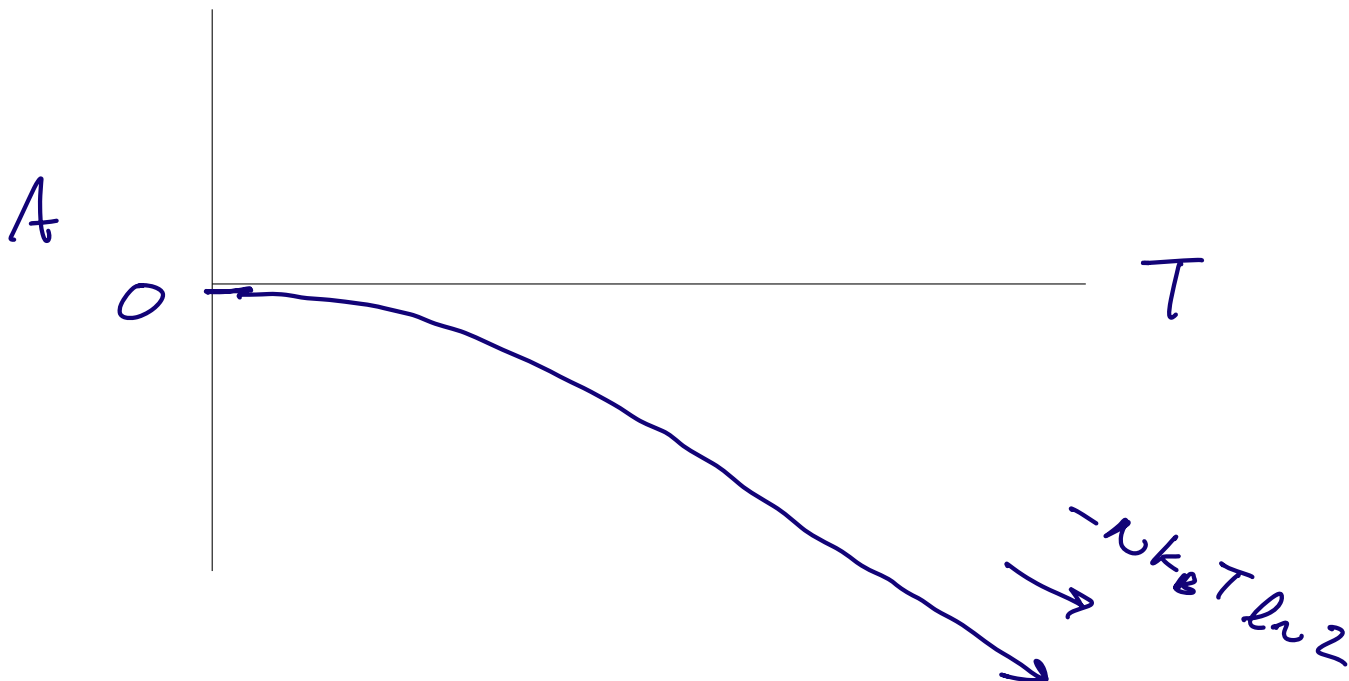$$q(\beta) = e^{-0\beta} + e^{-\varepsilon\beta} = 1 + e^{-\varepsilon\beta}$$

**2.2**   (4 pts) Sketch the partition function $q(\beta)$ as a function of $T$. Be sure to indicate values in the limits of low and high $T$.

$$
\begin{array}{l}
2 \\
\\
1
\end{array}
$$

$T=0$        $T \rightarrow$        $T \rightarrow \infty$

$\beta \rightarrow \infty$        $\leftarrow \beta = 1/T$        $\beta \rightarrow 0$

2.3 (6 pts) Sketch the Helmholtz (free) energy of the box as a function of $T$.

$$A = -Nk_B T \ln q_z$$



2.4 (6 pts) Derive an expression for the internal energy of the box as a function of $\beta$ and $N$.

$$U = -N\left(\frac{\partial \ln q_z}{\partial \beta}\right) = -\frac{N}{q_z}\frac{\partial q_z}{\partial \beta}$$

$$= -\frac{N}{q_z}\left(-\varepsilon e^{-\varepsilon\beta}\right) = \frac{N\varepsilon e^{-\varepsilon\beta}}{1 + e^{-\varepsilon\beta}}$$

2.5   (4 pts) What is the internal energy of the box in the limit that $\beta \to 0$, ie $T \to \infty$?

$$\frac{N}{2}\varepsilon$$

2.6   (4 pts) What is the entropy of the box in the limit that $\beta \to 0$, ie $T \to \infty$?

$$A = U - TS \quad \to \quad S = \frac{U - A}{T}$$

$$Z \to \quad S = \frac{\frac{N\varepsilon}{2} + Nk_B T \ln 2}{T}$$

$$= N\left\{ \frac{\varepsilon}{2T}^{\,0} + k_B \ln 2 \right\}$$

$$= N k_B \ln 2$$

Could derive from fact that there are 2 possible energy states.

**Table 1:** Key units in Physical Chemistry

| | | | | |
|---|---|---|---|---|
| $N_{\text{Av}}$: | $6.02214 \times 10^{23}$ | $\text{mol}^{-1}$ | | |
| 1 amu: | $1.6605 \times 10^{-27}$ | kg | | |
| $k_{\text{B}}$: | $1.38065 \times 10^{-23}$ | $\text{J K}^{-1}$ | $8.61734 \times 10^{-5}$ | $\text{eV K}^{-1}$ |
| $R$: | $8.314472$ | $\text{J K}^{-1} \text{ mol}^{-1}$ | $8.2057 \times 10^{-2}$ | $\text{l atm mol}^{-1} \text{ K}^{-1}$ |
| $\sigma_{\text{SB}}$: | $5.6704 \times 10^{-8}$ | $\text{J s}^{-1} \text{ m}^{-2} \text{ K}^{-4}$ | | |
| $c$: | $2.99792458 \times 10^{8}$ | $\text{m s}^{-1}$ | | |
| $h$: | $6.62607 \times 10^{-34}$ | $\text{J s}$ | $4.13566 \times 10^{-15}$ | $\text{eV s}$ |
| $\hbar$: | $1.05457 \times 10^{-34}$ | $\text{J s}$ | $6.58212 \times 10^{-16}$ | $\text{eV s}$ |
| $hc$: | $1239.8$ | $\text{eV nm}$ | | |
| $e$: | $1.60218 \times 10^{-19}$ | $\text{C}$ | | |
| $m_e$ : | $9.10938215 \times 10^{-31}$ | kg | 1: $0.5109989$ | $\text{MeV c}^{-2}$ |
| $\epsilon_0$: | $8.85419 \times 10^{-12}$ | $\text{C}^2 \text{ J}^{-1} \text{ m}^{-1}$ | $5.52635 \times 10^{-3}$ | $e^2 \text{ Å}^{-1} \text{ eV}^{-1}$ |
| $e^2/4\pi\epsilon_0$: | $2.30708 \times 10^{-28}$ | $\text{J m}$ | $14.39964$ | $\text{eV Å}$ |
| $a_0$: | $0.529177 \times 10^{-10}$ | m | $0.529177$ | Å |
| $E_{\text{H}}$: | $1$ | Ha | $27.212$ | eV |

# 3   Tables

**Table 2:** The new physics

| | |
|---|---|
| Stefan-Boltzmann Law | $\int I(\lambda, T)d\lambda = \sigma_{\mathrm{SB}}T^4$ |
| Wien's Law | $\lambda_{\mathrm{max}}T = 2897768$ nm K |
| Rayleigh-Jeans eq | $I(\lambda, T) = \dfrac{8\pi}{\lambda^4}k_B T c$ |
| Blackbody irradiance | $I(\lambda, T) = \dfrac{8\pi}{\lambda^5}\dfrac{hc^2}{e^{hc/\lambda k_B T} - 1}$ |
| Einstein crystal | $C_v = 3R\left(\dfrac{h\nu}{k_B T}\right)^2 \dfrac{e^{h\nu/k_B T}}{\left(e^{h\nu/k_B T} - 1\right)^2}$ |
| Photon energy | $\epsilon = h\nu$ |
| Rydberg equation | $\nu = R_H c\left(1/n^2 - 1/k^2\right)$ |
| Bohr equations $n = 1, 2, \ldots$ | $l_n = n\hbar$ <br> $r_n = n^2\left(\dfrac{4\pi\epsilon_0\hbar^2}{e^2 m_e}\right) = n^2 a_0$ <br> $E_n = -\dfrac{m_e e^4}{8\epsilon_0^2 h^2}\dfrac{1}{n^2} = -\dfrac{E_H}{2}\dfrac{1}{n^2}$ <br> $p_n = \dfrac{e^2}{4\pi\epsilon_0}\dfrac{m_e}{\hbar}\dfrac{1}{n} = p_0\dfrac{1}{n}$ |
| de Broglie equation | $\lambda = h/p$ |

**Table 3:** Postulates of Non-relativistic Quantum Mechanics

**Postulate 1: The physical state of a system is completely described by its wavefunction $\Psi$.** In general, $\Psi$ is a complex function of the spatial coordinates and time. $\Psi$ is required to be:

Single-valued

continuous and twice differentiable

square-integrable ($\int \Psi^* \Psi d\tau$ is defined over all finite domains)

For bound systems, $\Psi$ can always be normalized such that $\int \Psi^* \Psi d\tau = 1$

**Postulate 2:** To every physical observable quantity $M$ there corresponds a Hermitian operator $\hat{M}$. **The only observable values of $M$ are the eignevalues of $\hat{M}$.**

| Physical quantity | Operator | Expression |
|---|---|---|
| Position $x, y, z$ | $\hat{x}, \hat{y}, \hat{z}$ | $x\cdot, y\cdot, z\cdot$ |
| Linear momentum $p_x, \ldots$ | $\hat{p}_x, \ldots$ | $-i\hbar\dfrac{\partial}{\partial x}, \ldots$ |
| Angular momentum $l_x, \ldots$ | $\hat{p}_x, \ldots$ | $-i\hbar\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y}\right), \ldots$ |
| Kinetic energy $T$ | $\hat{T}$ | $-\dfrac{\hbar^2}{2m}\nabla^2$ |
| Potential energy $V$ | $\hat{V}$ | $V(\mathbf{r}, t)$ |
| Total energy $E$ | $\hat{H}$ | $-\dfrac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t)$ |

**Postulate 3:** If a particular observable $M$ is measured many times on many identical systems is a state $\Psi$, the average resuts with be the expectation value of the operator $\hat{M}$:

$$\langle M \rangle = \int \Psi^* (\hat{M}\Psi) d\tau$$

**Postulate 4:** The energy-invariant states of a system are solutions of the equation

$$\hat{H}\Psi(\mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t)$$
$$\hat{H} = \hat{T} + \hat{V}$$

The time-independent, stationary states of the system are solutions to the equation

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r})$$

**Postulate 5:** (The **uncertainty principle**.) Operators that do not commute ($\hat{A}(\hat{B}\Psi) \neq \hat{B}(\hat{A}\Psi)$) are called *conjugate*. Conjugate observables cannot be determined simultaneously to arbitrary accuracy. For example, the standard deviation in the measured positions and momenta of particles all described by the same $\Psi$ must satisfy $\Delta x \Delta p_x \geq \hbar/2$.

**Table 4:** Equations of the Canoncial ($NVT$) Ensemble

| $\beta = 1/k_B T$ | Full Ensemble | Distinguishable particles (e.g. atoms in a lattice) | Indistinguishable particles (e.g. molecules in a fluid) |
|---|---|---|---|
| Single particle partition function | | $q(V,T) = \sum_i e^{-\epsilon_i \beta}$ | $q(V,T) = \sum_i e^{-\epsilon_i \beta}$ |
| Full partition function | $Q(N,V,T) = \sum_j e^{-U_j \beta}$ | $Q = q(V,T)^N$ | $Q = q(V,T)^N / N!$ |
| Log partition function | $\ln Q$ | $N \log q$ | $N \ln q - \ln N!$ $\approx N(\ln Q - \ln N + 1)$ |
| Helmholtz energy ($A = U - TS$) | $-\dfrac{\ln Q}{\beta}$ | $-\dfrac{N \ln q}{\beta}$ | $-\dfrac{N}{\beta}\left(\ln\dfrac{q}{N} + 1\right)$ |
| Internal energy ($U$) | $-\left(\dfrac{\partial \ln Q}{\partial \beta}\right)_{NV}$ | $-N\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V$ | $-N\left(\dfrac{\partial \ln q}{\partial \beta}\right)_V$ |
| Pressure ($P$) | $\dfrac{1}{\beta}\left(\dfrac{\partial \ln Q}{\partial V}\right)_{N\beta}$ | $\dfrac{N}{\beta}\left(\dfrac{\partial \ln q}{\partial V}\right)_\beta$ | $\dfrac{N}{\beta}\left(\dfrac{\partial \ln q}{\partial V}\right)_\beta$ |
| Entropy ($S/k_B$) | $\beta U + \ln Q$ | $\beta U + N \ln q$ | $\beta U + N\left(\ln(q/N) + 1\right)$ |
| Chemical potential ($\mu$) | $-\dfrac{1}{\beta}\left(\dfrac{\partial \ln Q}{\partial N}\right)_{VT}$ | $-\dfrac{\ln q}{\beta}$ | $-\dfrac{\ln(q/N)}{\beta}$ |

**NOTE!** All energies are referenced to their values at 0 K. Enthalpy $H = U + PV$, Gibb's Energy $G = A + PV$.