Operator $\hat{H}$ of the total energy

Many-body Hamiltonian $\hat{H}$:

$$\hat{H} = \hat{T} \pm V(\underline{R}) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N} V(r_{ij}) \quad (3)$$

$$\hat{H}\psi(\underline{R}) = \left\{\hat{T} + V(\underline{R})\right\}\psi(\underline{R}) = \hat{T}\psi(\underline{R}) + V(\underline{R})\psi(\underline{R})$$

$$= -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2\psi(\underline{R}) + \sum_{i=1}^{N} V(r_{ij})\psi(\underline{R})$$

Stationary (time-independent) many-body Schrödinger equation.

Eigenvalue equation for the energy eigenvalues E_n and eigenfunctions $\phi_n(\underline{R}) = \phi_n(\underline{r}_1, \underline{r}_2, ..., \underline{r}_N)$ of the many-body Hamiltonian $\hat{H}$ (eq. 3)

$$\hat{H}\phi_n(\underline{R}) = E_n\phi_n(\underline{R}) \quad (4)$$

Index n simply numerates the distinct energy eigenfunctions $\phi_n(\underline{R})$. Absolute ground state of the many-body system at temperature $T = 0$ is denoted by $n = 0$. E_0 is the ground-state energy, and $\phi_0(\underline{R})$ is the ground state wavefunction.

$E_0 < E_n$ for al other excited states. Ground state is energy eigenstate with the lowest energy eigenvalues.

$$\langle k|n\rangle = \int_{V^N} \phi_k{}^*(\underline{R})\phi_n(\underline{R})d\underline{R}$$

$$= \int_V\int_V ... \int_V \phi_k{}^*(\underline{r}_1, \underline{r}_2, ..., \underline{r}_N)\phi_n(\underline{r}_1, \underline{r}_2, ..., \underline{r}_N)d\underline{r}_1 d\underline{r}_2 ... dr_N$$

There are N 3-dimensional integrals, integrating over $\underline{r}_1$, $\underline{r}_2$, …, $\underline{r}_N$.

$$\langle k|n\rangle = \int_V\int_V ... \int_V \phi_k{}^*(\underline{R})\phi_n(\underline{R})dx_1dy_1dz_1dx_2dy_2dz_2...dx_Ndy_Ndz_N$$

The above is the scalar product of $\phi_k(\underline{R})$ and $\phi_n(\underline{R})$. $3N$-dimensional volume integral or N three-dimensional volume integrations, where $\underline{r}_i$ is integrated over the three-dimensional volume V occupied by the many-particle system.

$$\begin{aligned}\langle k|\hat{H}|n\rangle &= \int_{V^N} \phi_k{}^*(\underline{R})\left[\hat{H}\phi_n(\underline{R})\right]d\underline{R} \\ &= \int_{V^N} \left[\hat{H}\phi_k(\underline{R})\right]^*\phi_n(\underline{R})d\underline{R}\end{aligned} \quad (6)$$

As Hamiltonian is self-adjoint (Hermitian , symmetric). The asterisk denotes complex conjugation.

$$\psi(\underline{R}) = \mathrm{Re}\{\psi(\underline{R})\} + i\,\mathrm{Im}\{\psi(\underline{R})\}$$

$$\psi(\underline{R})^* = \mathrm{Re}\{\psi(\underline{R})\} - i\,\mathrm{Im}\{\psi(\underline{R})\}$$

Multiply (4) with $\phi_k{}^*(\underline{R})$ and integrate over $\underline{R}$:

$$\phi_k{}^*(\underline{R})\hat{H}\phi_n(\underline{R}) = E_n\phi_k{}^*(\underline{R})\phi_n(\underline{R})$$

$$\int_{V^N}\phi_k{}^*(\underline{R})\hat{H}\phi_n(\underline{R})d\underline{R} = E_n\int_{V^N}\phi_k{}^*(\underline{R})\phi_n(\underline{R})d\underline{R}$$

Using equations (5) and (6),

$$\langle k|\hat{H}|n\rangle = E_n\langle k|n\rangle$$

$$\hat{H}\phi_k(\underline{R}) = E_n\phi_k(\underline{R})$$
$$\hat{H}\phi_k{}^*(\underline{R}) = E_n\phi_k{}^*(\underline{R})$$

So $\hat{H}$, equation (3), is real.

All eigenvalues E_n of $\hat{H}$ are real, since $\hat{H}$ is self-adjoint.
$E_n{}^* = E_n$

$$\int_{V^N}\left[\hat{H}\phi_k{}^*(\underline{R})\right]\phi_n(\underline{R})d\underline{R} = \int_{V^N}\left[\hat{H}\phi_k(\underline{R})\right]^*\phi_n(\underline{R})d\underline{R} = \langle k|\hat{H}|n\rangle$$
$$= E_k\int_{V^N}\phi_k{}^*(\underline{R})\phi_n(\underline{R})d\underline{R} = E_k\langle k|n\rangle$$
$$\therefore E_k\langle k|n\rangle = \langle k|\hat{H}|n\rangle$$
$$\therefore (E_n - E_k)\langle k|n\rangle = 0$$
$$\langle k|n\rangle = 0 \text{ for } E_n \neq E_k$$

Eigenfunctions of different eigenvalues are orthogonal.

In general, degeneracy (different eigenfunctions have same energy eigenvalues).

Eigenfunctions can always be made orthogonal to each other by means of the Gram-Schmidt orthogonalization method. From now on always assume that eigenfunctions $\phi_n(\underline{R})$ of $\hat{H}$ form a complete normalized orthogonal system of basis functions of the Hilbert space.

Orthogonality: $\langle k|n\rangle = 0$ for $k \neq n$
Normalization: $\langle n|n\rangle = \int_{V^N}\left|\phi_n(\underline{R})^2\right|d\underline{R} = 1$
If $\tilde{\phi}_n(\underline{R})$ is not normalized, then $\phi_n(\underline{R})$:

$$\phi_n(\underline{R}) = \frac{\tilde{\phi}_n(\underline{R})}{\sqrt{\langle\tilde{\phi}_n|\tilde{\phi}_n\rangle}}$$
$$\langle\tilde{\phi}_n|\tilde{\phi}_n\rangle = \int_{V^N}\left|\tilde{\phi}_n(\underline{R})\right|d\underline{R}$$

Orthonormalised: $\langle k|n\rangle = \delta_{kn}$ (7)

Kronecker delta $\delta_{kn} = \begin{cases} 0 & k \neq n \\ 1 & k = n \end{cases}$

Completeness: any wave function $\psi(\underline{R})$ may be expanded in terms of $\phi_{n(\underline{R})}$.

$$\psi(\underline{R}) = \sum_n c_n\phi_n(\underline{R})$$

Multiply with $\phi_k{}^*(\underline{R})$ and integrate,

$$\int_{V^N}\phi_k{}^*(\underline{R})\psi(\underline{R})d\underline{R} = \langle k|\psi\rangle = \sum_n c_n\int_{V^N}\phi_k{}^*(\underline{R})\phi_n(\underline{R})d\underline{R}$$
$$= \sum_n c_n\langle k|n\rangle = \sum_n c_n\delta_{kn}$$
$$c_k = \langle k|\psi\rangle \rightarrow c_n = \langle n|\psi\rangle$$

$$\psi(\underline{R}) = \sum_n \langle n|\psi\rangle \phi_n(\underline{R})$$

$$\langle n|\psi\rangle = \int_{V^N} \phi_n{}^*(\underline{R})\psi(\underline{R})d\underline{R} \quad (8)$$

1.2 The Many-Body Density Operator

Temperature $T > 0$, $\beta = \frac{1}{k_B T}$

$$\hat{W} = \frac{1}{Z}e^{-\beta\hat{H}} \quad (9)$$

This is the density operator. Z is the partition function, and is also known as the sum of states.

$$e^{-\beta\hat{H}}\phi_n(\underline{R}) = e^{-\beta E_n}\phi_n(\underline{R}) \quad (10)$$

where $\hat{H}\phi_n(\underline{R}) = E_n\phi_n(\underline{R})$. The eigenfunctions of $e^{-\beta\hat{H}}$ are the eigenfunctions $\phi_n(\underline{R})$ of $\hat{H}$ and its eigenvalues are $e^{-\beta E_n}$.

$$\begin{aligned} e^{-\beta\hat{H}}\psi(\underline{R}) &= e^{-\beta\hat{H}}\sum_n \langle n|\psi\rangle \phi_n(\underline{R}) \\ &= \sum_n \langle n|\psi\rangle e^{-\beta\hat{H}}\phi_n(\underline{R}) \\ &= \sum_n \langle n|\psi\rangle e^{-\beta E_n}\phi_n(\underline{R}) \end{aligned}$$

$$e^{-\beta\hat{H}}\psi(\underline{R}) = \sum_n e^{-\beta E_n}\langle n|\psi\rangle \phi_n(\underline{R}) \quad (11)$$

$$Z = Tr\left\{e^{-\beta\hat{H}}\right\}$$

where $Tr\{\ \}$ denotes the trace, i.e. the sum of eigenvalues (energies).

$$Z = \sum_n e^{-\beta E_n} \quad (12)$$

$$\hat{W}\phi_n(\underline{R}) = \frac{e^{-\beta E_n}}{Z}\phi_n(\underline{R}) \quad (13)$$

Eigenvalues of the canonical density operator $\hat{W}$ are given by $\frac{e^{-\beta E_n}}{Z}$.

$$Tr\left(\hat{W}\right) = \sum_n \frac{e^{-\beta E_n}}{Z} = \frac{1}{Z}\sum_n e^{-\beta E_n} = 1$$

This gives unit-normalization of the density operator.

Macroscopic thermodynamics (statistical physics) may be obtained from Z, e.g.

$$F = E - TS = -k_B T\ln(Z)$$

where F is the Helmholtz free energy, $E = E_{kin} + E_{pot}$ is the total energy and S is the entropy.