DENSITY MATRICES AND TOTAL ENERGY - PURE STATES

First-order density matrix

$x_i = \vec{r}_i \sigma_i$

$$\gamma_1(\vec{r}_1'\sigma_1'; \vec{r}_1\sigma_1) = N \int dx_2 \ldots dx_N \sum_{\sigma_2 \ldots \sigma_N} \Psi^*(x_1', x_2 \ldots x_N)\, \Psi(x_1, x_2 \ldots x_N)$$

[(anti)symmetric + normalized]

spinless form
$$\gamma(\vec{r}_1', \vec{r}_1) = \sum_{\sigma} \gamma_1(\vec{r}_1\sigma_1'; \vec{r}_1\sigma_1)$$

particle density
$$\rho(\vec{r}) = \gamma(\vec{r}, \vec{r}), \quad \int dr\, \rho(r) = N$$

Second-order density matrix

$\binom{N}{2}$

$$\Gamma_2(\vec{r}_1'\sigma_1'; \vec{r}_2'\sigma_2'; \vec{r}_1\sigma_1; \vec{r}_2\sigma_2) = \frac{N(N-1)}{2} \cdot \int dr_3 \ldots dr_N \sum_{\sigma_3 \ldots \sigma_N} \cdot$$
$$\Psi^*(r_1'\sigma_1', r_2'\sigma_2', \ldots, r_N\sigma_N)\, \Psi(r_1\sigma_1, r_2\sigma_2, \ldots, r_N\sigma_N)$$

spinless form

$$\Gamma(\vec{r}_1', \vec{r}_2'; \vec{r}_1, \vec{r}_2) = \sum_{\sigma_1\sigma_2} \Gamma_2(\vec{r}'\sigma_1'; \vec{r}_2'\sigma_2'; \vec{r}_1\sigma_1; \vec{r}_2\sigma_2)$$

k-order density matrix

$$\Gamma_k(\vec{r}_1'\sigma_1' \ldots \vec{r}_k'\sigma_k'; \vec{r}_1\sigma_1 \ldots \vec{r}_k\sigma_k) = \binom{N}{k} \sum_{\sigma_{k+1} \ldots \sigma_N} \int dx_{k+1} \ldots dx_N$$
$$\Psi^*(\vec{r}_1'\sigma_1' \ldots \vec{r}_k'\sigma_k'; \vec{r}_{k+1}\sigma_{k+1} \ldots \vec{r}_N\sigma_N) \cdot$$
$$\Psi(\vec{r}_1\sigma_1 \ldots \vec{r}_k\sigma_k; \vec{r}_{k+1}\sigma_{k+1} \ldots \vec{r}_N\sigma_N)$$

$$E = \int dx_1 \ldots dx_N \, \Psi^*(x_1 \ldots x_N) \Big[\overbrace{-\frac{\hbar^2}{2m} \sum_{i=1}^{N} \partial^2_{x_i}}^{(\mathrm{I})} + \overbrace{\sum_{i=1}^{N} U(x_i)}^{(\mathrm{II})} +$$

$$+ \underbrace{\frac{1}{2} \sum_{i,j=1}^{N} V(x_i - x_j)}_{(\mathrm{III})} \Big] \Psi(x_1 \ldots x_N)$$

$$(\mathrm{II}) = \sum_{i=1}^{N} \int dx_1 \ldots dx_N \, \Psi^*(x_1 \ldots x_N) \, U(x_i) \, \Psi(x_1 \ldots x_N) =$$

$$= \int dx_1 \, U(x_1) \int dx_2 \ldots dx_N \, \Psi^*(x_1 \ldots x_N) \Psi(x_1 \ldots x_N) +$$

$$+ \int dx_2 \, u(x_2) \int dx_1 \, dx_3 \ldots dx_N \, \Psi^*(x_1 \ldots x_N) \Psi(x_1 \ldots x_N) + \ldots =$$

$\{ x_1 \leftrightarrow x_2 \}$ N-terms together

$$= N \int dx_1 \, U(x_1) \int dx_2 \ldots dx_N \, \Psi^*(x_1 \ldots x_N) \Psi(x_1 \ldots x_N) =$$

$$= \int dx_1 \, U(x_1) \underbrace{\gamma(x_1, x_1)}_{\rho(x_1)} = \int dx_1 \, U(x_1) \rho(x_1)$$

$$(\mathrm{I}) = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \int dx_1 \ldots dx_N \, \Psi^*(x_1 \ldots x_N) \, \partial^2_{x_i'} \Psi(x_1' \ldots x_N') \Big|_{x_i = x_i'} =$$

$$= -\frac{\hbar^2}{2m} \Big[\int dx_1 \, \partial^2_{x_1'} \int dx_2 \ldots dx_N \, \Psi^*(x_1 \ldots x_N) \Psi(x_1' \ldots x_N') \Big|_{x_i = x_i'} +$$

$$\int dx_2 \, \partial^2_{x_2'} \int dx_1 \, dx_3 \ldots dx_N \, \Psi^*(x_1 x_2 \ldots x_N) \Psi(x_1' x_2' \ldots x_N') \Big|_{x_i = x_i'} + \ldots \Big]$$

$x_1 \leftrightarrow x_2$ N-terms together

$$= -\frac{\hbar^2}{2m} \Big[N \int dx_1 \, \partial^2_{x_1'} \int dx_2 \ldots dx_N \, \Psi^*(x_1 x_2 \ldots x_N) \Psi(x_1' x_2 \ldots x_N) \Big|_{x_1 = x_1'} \Big] =$$

$$= -\frac{\hbar^2}{2m} \int dx_1 \left[\partial^2_{x_1'} \gamma(x_1, x_1') \right] \Big|_{x_1 = x_1'}$$

$$(\mathrm{iii}) = \frac{1}{2}\sum_{i\neq j}\int dx_1 \dots dx_N \; V(x_i - x_j)\,\Psi^*(x_1 \dots x_N)\,\Psi(x_1 \dots x_N) =$$

$$= \frac{1}{2}\Big[\int dx_1 \sum_{j\neq 1} \int dx_2 \dots dx_N \; V(x_1 - x_j)\,\Psi^*(x_1 \dots x_N)\,\Psi(x_1 \dots x_N) +$$

$$\int dx_2 \sum_{j\neq 2} \int dx_1\, dx_3 \dots dx_N \; V(x_2 - x_j)\,\Psi^*(x_1 \dots x_N)\,\Psi(x_1 \dots x_N) + \dots\Big]$$

N - terms together

$$= \frac{1}{2}\Big[\int dx_1 \int dx_2 \int dx_3 \dots dx_N \; V(x_1 - x_2)\,\Psi^*(x_1 \dots x_N)\,\Psi(x_1 \dots x_N) +$$

$$\int dx_1 \int dx_3 \int dx_2\, dx_4 \dots dx_N \; V(x_1 - x_3)\,\Psi^*(x_1 \dots x_N)\,\Psi(x_1 \dots x_N) +$$

$x_3 \Leftrightarrow x_2$ ... $(N-1)$ terms +

$$\int dx_2 \int dx_1 \int dx_3 \dots dx_N \; V(x_2 - x_1)\,\Psi^*(x_1 \dots x_N)\,\Psi(x_1 \dots x_N) + \dots$$

$N-1$ terms

$$+ \vdots \quad \Big] =$$

$$= \frac{1}{2} N(N-1) \int dx_1 \int dx_2 \; V(x_1 - x_2)\,\Gamma(x_1 x_2 ; x_1 x_2)$$

$$\boxed{\begin{aligned} E = & -\frac{\hbar^2}{2m}\int dx \left[\partial_x^2\, \gamma(x', x)\big|_{x=x'}\right] + \\ & + \int dx\; U(x)\,\rho(x) + \\ & + \frac{1}{2}\int dx\, dy\; V(x-y)\,\Gamma(x y ; x y) \end{aligned}}$$

Only one and two particle matrices are needed to get a total energy of the interacting system via pair wise potential.

Relation to mixed states

$$\hat{\rho}_p = |\Psi\rangle\langle\Psi| \quad \text{pure}$$
$$\hat{\rho}_m = \sum_\alpha p_\alpha |\Psi_\alpha\rangle\langle\Psi_\alpha| \quad \text{mixed}$$
} statistical operators

density matrix

$$\langle x_1' \ldots x_N' | \hat{\rho}_p | x_1 \ldots x_N\rangle = \langle x_1' \ldots x_N' |\Psi\rangle\langle\Psi| x_1 \ldots x_N\rangle =$$
$$= \Psi^*(x_1' \ldots x_N')\, \Psi(x_1 \ldots x_N)$$

$$\langle x_1' \ldots x_N' | \hat{\rho}_m | x_1 \ldots x_N\rangle = \sum_\alpha p_\alpha \Psi_\alpha^*(x_1' \ldots x_N')\, \Psi_\alpha(x_1 \ldots x_N)$$

$\downarrow$ one-particle (reduced) density matrix

$$\gamma_m(x_1', x_1) = N \sum_\alpha p_\alpha \int dx_2 \ldots dx_N\, \Psi_\alpha^*(x_1' x_2 \ldots x_N)\, \Psi(x_1 x_2 \ldots x_N)$$

two-particle (reduced) density matrix

$$\Gamma(x_1' x_2'; x_1 x_2) = \frac{N(N-1)}{2} \sum_\alpha p_\alpha \int dx_3 \ldots dx_N\, \Psi_\alpha^*(x_1' x_2' x_3 \ldots x_N)\, \Psi(x_1 x_2 \ldots x_N)$$