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Equivalence of functionals for the electron gas and jellium at finite temperature

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Motivation

- Development of electron functionals for orbital free density functional theory (DFT).
- Application of DFT to electron component of ion – electron systems for ab initio molecular dynamics simulations.
- Connection to QMC for jellium

Objective

- Precise relationship of electron gas functionals to those of model system jellium (general non-uniform states).

Take away

- Can limit attention to “simpler” jellium system for DFT

Inhomogeneous electron gas at equilibrium

$$\widehat{H}_e + \widehat{U}_{ex} = \sum_{\alpha=1}^{N} \frac{\widehat{p}_\alpha^2}{2m} + \frac{1}{2}e^2 \int d\mathbf{r}d\mathbf{r}' \frac{\widehat{n}(\mathbf{r})\widehat{n}(\mathbf{r}') - \widehat{n}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r} v_{ex}(\mathbf{r})\widehat{n}(\mathbf{r})$$

number density operator $\widehat{n}(\mathbf{r}) = \sum_{\alpha=1}^{N} \delta(\mathbf{r} - \widehat{\mathbf{q}}_\alpha)$

Thermodynamics at given $\beta, V, \mu(\mathbf{r}) \equiv \mu - v_{ex}(\mathbf{r})$ **(local chemical potential)**

$$\beta\Omega_e[\beta, V \mid \mu] = -\beta p_e[\beta, V \mid \mu] V \equiv -\ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta\left(\widehat{H}_e - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right)}$$

Inhomogeneous jellium at equilibrium

$$\widehat{H}_j + \widehat{U}_{ex} = \sum_{\alpha=1}^{N} \frac{\widehat{p}_\alpha^2}{2m} + \frac{1}{2}e^2 \int d\mathbf{r}d\mathbf{r}' \frac{(\widehat{n}(\mathbf{r}) - n_b)(\widehat{n}(\mathbf{r}') - n_b) - \widehat{n}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \int d\mathbf{r} v_{ex}(\mathbf{r})\widehat{n}(\mathbf{r})$$

Same thermodynamic state $\beta, V, \mu(\mathbf{r})$.

$$\beta\Omega_j[\beta, V, n_b \mid \mu] = -\beta p_j[\beta, V, n_b \mid \mu] V = -\ln \sum_{N=0}^{\infty} Tr^{(N)} e^{-\beta\left(\widehat{H}_j - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right)}$$

Different functionals $\Omega_e[\beta, V \mid \cdot]$ **and** $\Omega_j[\beta, V \mid \cdot]$ **characterized by** $\widehat{H}_e$ **and** $\widehat{H}_j$ **, respectively**

Jellium is electron gas with "special" external potential

$$\widehat{H}_j = \widehat{H}_e + \int d\mathbf{r} v_b(\mathbf{r}, n_b)\, \widehat{n}(\mathbf{r}) \qquad v_b(\mathbf{r}, n_b) = -e^2 \int d\mathbf{r}' \frac{n_b}{|\mathbf{r} - \mathbf{r}'|} + \epsilon_b$$

$$\Downarrow$$

$$\beta\Omega_j[\beta, V \mid \mu] = \beta\Omega_e[\beta, V \mid \mu - v_b]$$

and in general, same relation for other average properties

$$X_e[\beta, V \mid \mu] = \sum_{N=0}^{\infty} Tr^{(N)} \widehat{\rho}_e \widehat{X}, \qquad \widehat{\rho}_e = e^{\beta\Omega_e[\beta,V|\mu]} e^{-\beta\left(\widehat{H}_e - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right)}$$

$$X_j[\beta, V \mid \mu] = \sum_{N=0}^{\infty} Tr^{(N)} \widehat{\rho}_j \widehat{X}, \qquad \widehat{\rho}_j = e^{\beta\Omega_j[\beta,V|\mu]} e^{-\beta\left(\widehat{H}_j - \int d\mathbf{r}\mu(\mathbf{r})\widehat{n}(\mathbf{r})\right)}$$

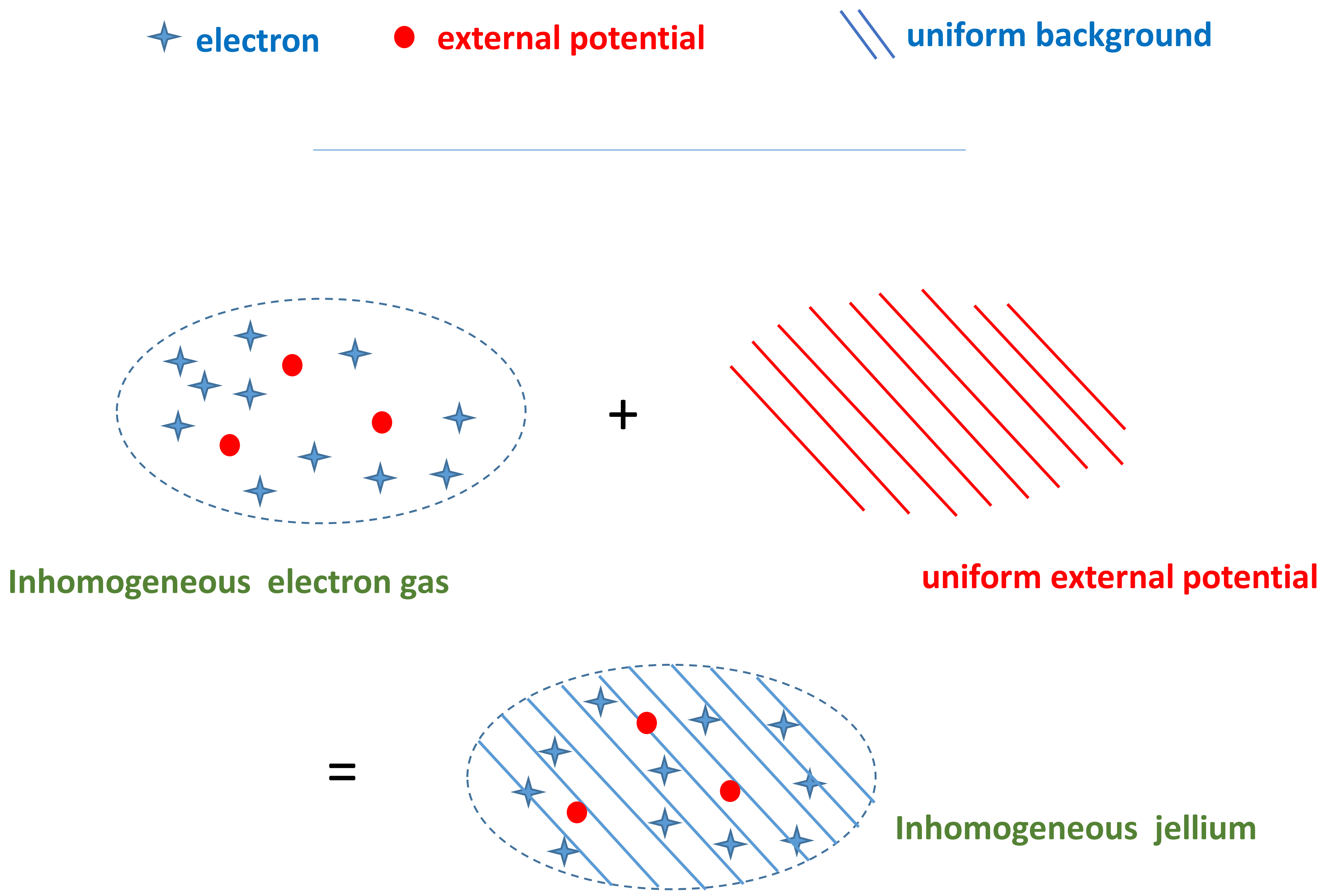
$$\Downarrow$$

$$X_j[\beta, V \mid \mu] = X_e[\beta, V \mid \mu - v_b]$$

Example: density (a derived property in this ensemble)

$$n_e(\mathbf{r}, \beta, V \mid \mu) = -\frac{\delta\beta\Omega_e[\beta, V \mid \mu]}{\delta\beta\mu(\mathbf{r})}\Big|_{\beta,V} \qquad n_j(\mathbf{r}, \beta, V, n_b \mid \mu) = -\frac{\delta\beta\Omega_j[\beta, V \mid \mu]}{\delta\beta\mu(\mathbf{r})}\Big|_{\beta,V,n_b}$$

$$n_j(\mathbf{r}, \beta, V, n_b \mid \mu) = n_e(\mathbf{r}, \beta, V \mid \mu - v_b)$$



electron
external potential
uniform background
Inhomogeneous electron gas
+
uniform external potential
=
Inhomogeneous jellium

Relationship of functionals of $\mu(\mathbf{r})$ is transparent. What about density functionals?

Change variables $\beta, V, \mu(\mathbf{r}) \to \beta, V, n(\mathbf{r})$ **via Legendre transform**

$$F_e[\beta, V \mid n_e] = \Omega_e[\beta, V \mid \mu] + \int d\mathbf{r}\mu(\mathbf{r})n_e(\mathbf{r}, \beta, V \mid \mu)$$

$$F_j[\beta, V, n_b \mid n_j] = \Omega_j[\beta, V, n_b \mid \mu] + \int d\mathbf{r}\mu(\mathbf{r})n_j(\mathbf{r},\beta, V, n_b \mid \mu)$$

$$\Downarrow$$

$$F_j[\beta, V, n_b \mid n_j] = \Omega_e[\beta, V \mid \mu - v_b] + \int d\mathbf{r}\,(\mu(\mathbf{r}) - v_b(\mathbf{r}, n_b))\, n_e(\mathbf{r},\beta, V \mid \mu - v_b)$$

$$+ \int d\mathbf{r} v_b(\mathbf{r}, n_b) n_e(\mathbf{r},\beta, V \mid \mu - v_b)$$

$$= F_e[\beta, V \mid n_e(\mid \mu - v_b)] + \int d\mathbf{r} v_b(\mathbf{r}, n_b) n_e(\mathbf{r},\beta, V \mid \mu - v_b)$$

$$= F_e[\beta, V \mid n_j] + \int d\mathbf{r} v_b(\mathbf{r}, n_b) n_j(\mathbf{r} \mid \mu)$$

$$F_j[\beta, V, n_b \mid n] = F_e[\beta, V \mid n] + \int d\mathbf{r} v_b(\mathbf{r}, n_b) n(\mathbf{r})$$

Equivalence of exchange–correlation density functionals

$$F = F_0 + F_H + F_{xc}$$

Hartree contributions

$$F_{eH}[\beta, V \mid n] = \frac{1}{2}e^2 \int d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$F_{jH}[\beta, V, n_b \mid n] = \frac{1}{2}e^2 \int d\mathbf{r}d\mathbf{r}' \frac{(n(\mathbf{r})-n_b)\,(n(\mathbf{r}')-n_b)}{|\mathbf{r}-\mathbf{r}'|}$$

$$\Downarrow$$

$$F_{eH}[\beta, V \mid n] + \int d\mathbf{r} v_b(\mathbf{r}) n(\mathbf{r}) = F_{jH}[\beta, V, n_b \mid n]$$

Equivalence of exchange- correlation functionals follows from previous slide

$$F_j[\beta, V, n_b \mid n] = F_e[\beta, V \mid n] + \int d\mathbf{r} v_b(\mathbf{r}, n_b) n(\mathbf{r})$$

$$\Downarrow$$

$$F_{jxc}[\beta, V, n_b \mid n] = F_{exc}[\beta, V \mid n]$$

Equivalence of total free energy density functionals

$$F^T(\beta, V \mid n) = F(\beta, V \mid n) + \int d\mathbf{r} v(\mathbf{r}) n(\mathbf{r})$$

total — **"intrinsic"**

$$F_j^T(\beta, V, n_b \mid n) = F_j(\beta, V, n_b \mid n) + \int d\mathbf{r} v_{ex}(\mathbf{r}) n(\mathbf{r})$$

$$F_e^T(\beta, V \mid n) = F_e(\beta, V \mid n) + \int d\mathbf{r} \left(v_{ex}(\mathbf{r}) + v_b(\mathbf{r}, n_b) \right) n(\mathbf{r})$$

$$\boxed{F_j^T(\beta, V, n_b \mid n) = F_e^T(\beta, V \mid n)}$$

Thermodynamic limit (extensive systems)

$$\lim_{V\to\infty} \frac{1}{V} F_j(\beta, V, n_b \mid n) \,|_{n, n_b = \overline{N}/V} \equiv f_j(\beta \mid n) \qquad \text{exists}$$

(Lieb and Narnhoffer, J. Stat. Phys. 12, 291 (1975))

$$\lim_{V\to\infty} \frac{1}{V} F_e(\beta, V \mid n) \,|_{n,} \qquad \text{does not exist (in general)}$$

electron Hartree contribution for uniform density does not scale linearly with the volume

$$F_{eH}[\beta, V \mid n] \;\to\; C\,(n_e e)^2\, V^{5/3}$$

Electron – ion systems

$$\beta\Omega(\beta,V,\mu_e,\mu_i) \equiv -\ln \sum_{N_e=0,N_i=0}^{\infty} Tr^{(N_e)} Tr^{(N_i)} e^{-\beta\left(\widehat{H}-\mu_e N_e-\mu_i N_i\right)}$$

$$\widehat{H} = \widehat{H}_e + \widehat{H}_i + U_{ie}$$

perform (formally) electron average

$$\beta\Omega(\beta,V,\mu_e,\mu_i) = -\ln \sum_{N_i=0}^{\infty} Tr^{(N_i)} e^{-\beta\left(\widehat{H}_i+\Omega_e(\beta,V|\mu_e)-\mu_i N_i\right)}$$

$$\beta\Omega_e(\beta,V \mid \mu_e) = -\ln \sum_{N_e=0}^{\infty} Tr^{(N_e)} e^{-\beta\left(\widehat{H}_e-\int d\mathbf{r}\mu_e(\mathbf{r})\widehat{n}_e(\mathbf{r})\right)} \qquad \mu_e(\mathbf{r}) \equiv \mu_e - \int d\mathbf{r}' \frac{-Ze^2\widehat{n}_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

(inhomogeneous electron gas)

Jellium representation

$$\widehat{H}_e + \widehat{H}_i + \widehat{U}_{ei} = \widehat{H}_{eJ} + \widehat{H}_{iJ} + \widehat{U}_{eiJ}$$

$$\beta\Omega(\beta,V,\mu_e,\mu_i) = -\ln \sum_{N_i=0}^{\infty} Tr^{(N_i)} e^{-\beta\left(\widehat{H}_{iJ}+\Omega_{eJ}(\beta,V|\mu_e)-\mu_i N_i\right)}$$

$$\beta\Omega_{eJ}(\beta,V \mid \mu_e) = -\ln \sum_{N_e=0}^{\infty} Tr^{(N_e)} e^{-\beta\left(\widehat{H}_{eJ}-\int d\mathbf{r}\mu_{eJ}(\mathbf{r})\widehat{n}_e(\mathbf{r})\right)} \qquad \mu_e(\mathbf{r}) = \mu_e - e^2 \int d\mathbf{r}' \frac{(-Z\widehat{n}_i(\mathbf{r}')+n_b)}{|\mathbf{r}-\mathbf{r}'|}$$

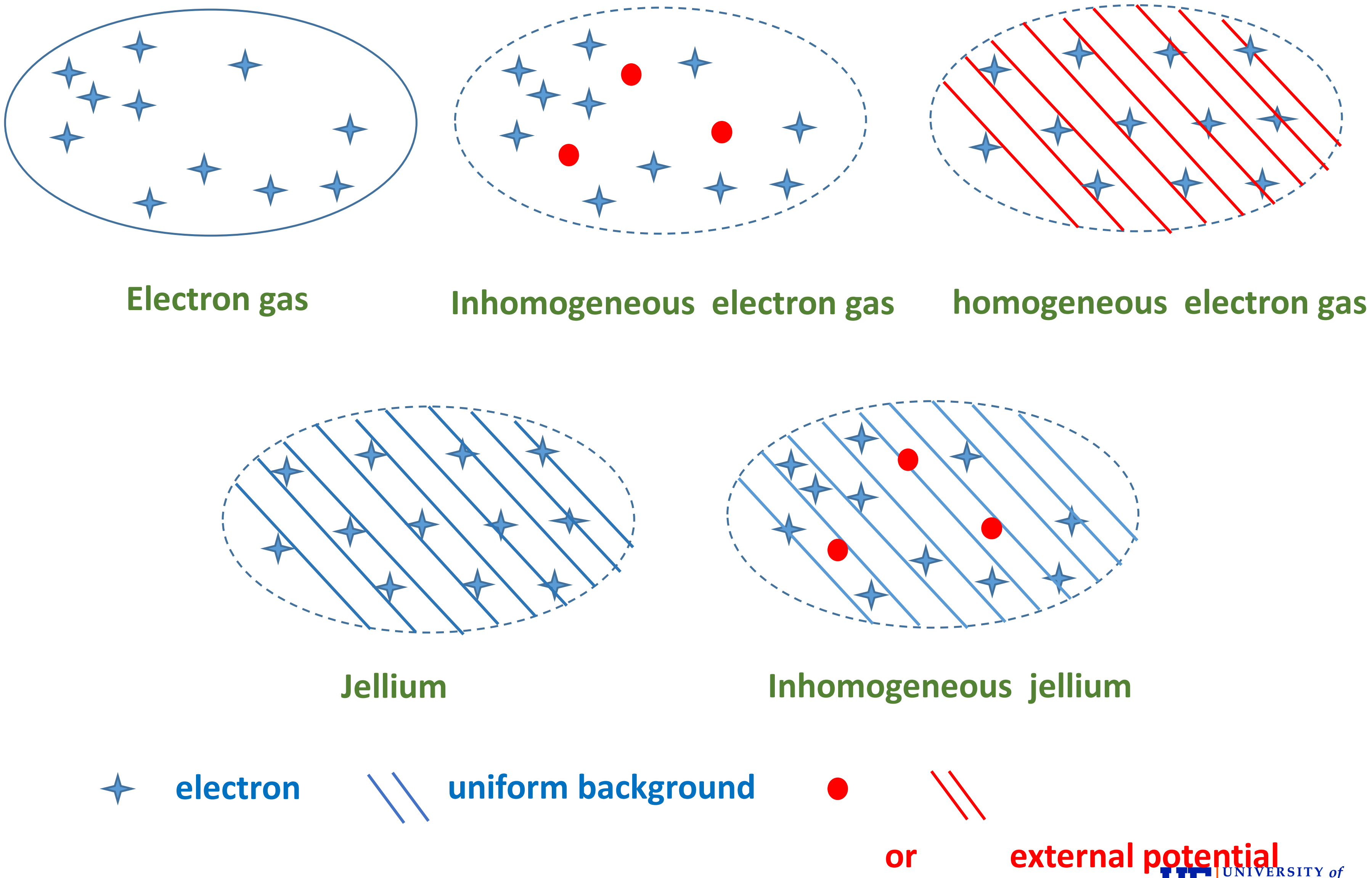
(inhomogeneous jellium)

Summary

- Electron exchange-correlation density functional is the same as that for jellium.

- Advantages of jellium for theoretical studies – charge neutral; thermodynamic limit exists; QMC simulations (presently for uniform state).

- Thermodynamics for ion-electron systems can be reformulated as coupled set of jelliums



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