Excited States of the Uniform Electron Gas

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Ground-State UEG [1–4]

Reduced energy of the UEG

$$\underbrace{\epsilon(\rho,\zeta)}_{\text{reduced energy}} = \underbrace{t_s(\rho,\zeta)}_{\text{kinetic}} + \underbrace{\epsilon_x(\rho,\zeta)}_{\text{exchange}} + \underbrace{\epsilon_c(\rho,\zeta)}_{\text{correlation}}$$

$$\underbrace{\rho}_{\text{density}} = \rho_\uparrow + \rho_\downarrow \quad \text{with} \quad \rho_\sigma = \int_0^{k_{F\sigma}} \frac{k^2}{2\pi^2}\,\mathrm{d}k = \frac{k_{F\sigma}^3}{6\pi^2}$$

Kinetic energy

$$t_{s\sigma}(\rho_\sigma) = \frac{1}{\rho_\sigma}\int_0^{\overbrace{k_{F\sigma}}^{\text{Fermi wave vector}}} \frac{k^2}{2}\frac{k^2}{2\pi^2}\,\mathrm{d}k = C_F\rho_\sigma^{2/3} \quad \text{with} \quad \underbrace{C_F}_{\text{Thomas-Fermi coefficient}} = -\frac{3}{10}(6\pi^2)^{2/3} \approx 4.5578$$

Exchange energy

$$\epsilon_{x\sigma}(\rho_\sigma) = \frac{1}{2}\iint \frac{\overbrace{\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)}^{\text{Fermi hole}}}{r_{12}}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2 = C_x\rho_\sigma^{1/3} \quad \text{with} \quad \underbrace{C_x}_{\text{Dirac coefficient}} = -\frac{3}{4}\left(\frac{6}{\pi}\right)^{1/3} \approx -0.930526$$

$$\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2) = -\frac{|\rho_1(\boldsymbol{r}_1,\boldsymbol{r}_2)|^2}{\rho(\boldsymbol{r}_1)} = -\frac{|j_{k_{F\sigma}}(r_{12})|^2}{\rho(\boldsymbol{r}_1)}$$

with $j_{k_{F\sigma}}(r_{12}) = 1/(2\pi^2)[\sin(k_{F\sigma}r_{12}) - k_{F\sigma}r_{12}\cos(k_{F\sigma}r_{12})]/(r_{12}^3)$.

Correlation energy

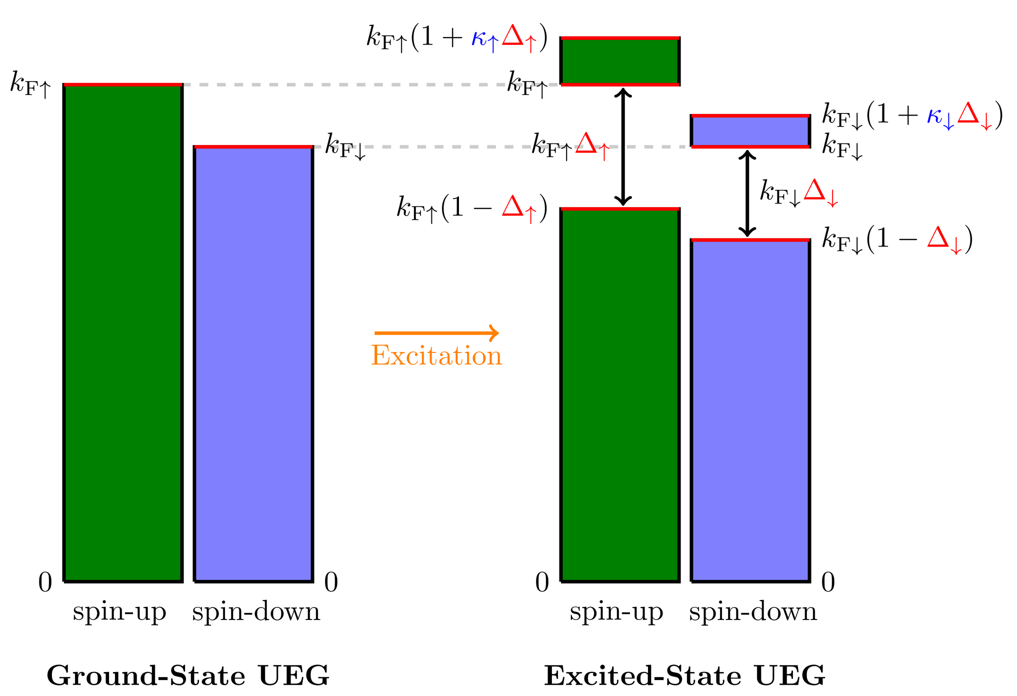
In the high-density limit (small r_s), we have

$$\epsilon_c(r_s,\zeta) = \lambda_0(\zeta)\ln r_s + \epsilon_0(\zeta) + \lambda_1(\zeta) r_s \ln r_s + \epsilon_1(\zeta) r_s + \cdots \qquad r_s = \left(\frac{3}{4\pi\rho}\right)^{1/3}$$

In the low-density limit (large r_s), we have

$$\epsilon_{xc}(r_s,\zeta) = \frac{\eta_0}{r_s} + \frac{\eta_1}{r_s^{3/2}} + \frac{\eta_2(\zeta)}{r_s^2} + \cdots \qquad \text{(Wigner crystal)}$$

Excited-State UEGs



Occupation

$$f_{k\sigma} = \begin{cases} 1 & 0 \le k \le k_{F\sigma}(1-\Delta_\sigma) \\ 0 & k_{F\sigma}(1-\Delta_\sigma) < k < k_{F\sigma} \\ 1 & k_{F\sigma} \le k \le k_{F\sigma}(1+\kappa_\sigma\Delta_\sigma) \\ 0 & k < k_{F\sigma}(1+\kappa_\sigma\Delta_\sigma) \end{cases}$$

Density

$$\rho_\sigma = \int_0^\infty f_{k\sigma}\frac{k^2}{2\pi^2}\,\mathrm{d}k = \int_0^{k_{F\sigma}(1-\Delta_\sigma)} \frac{k^2}{2\pi^2}\,\mathrm{d}k + \int_{k_{F\sigma}}^{k_{F\sigma}(1+\kappa_\sigma\Delta_\sigma)} \frac{k^2}{2\pi^2}\,\mathrm{d}k$$

$$= \left[1 - 3\Delta_\sigma(1-\kappa_\sigma) + 3\Delta_\sigma^2(1+\kappa_\sigma^2) - \Delta_\sigma^3(1-\kappa_\sigma^3)\right]\frac{k_{F\sigma}^3}{6\pi^2}$$

If one matches the density of the ground- and excited-state UEG, it yields

$$\boxed{\kappa_\sigma = \frac{(1+3\Delta_\sigma - 3\Delta_\sigma^2 + \Delta_\sigma^3)^{1/3} - 1}{\Delta_\sigma}}$$

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Kinetic and Exchange Energies of Excited-State UEGs

Kinetic energy

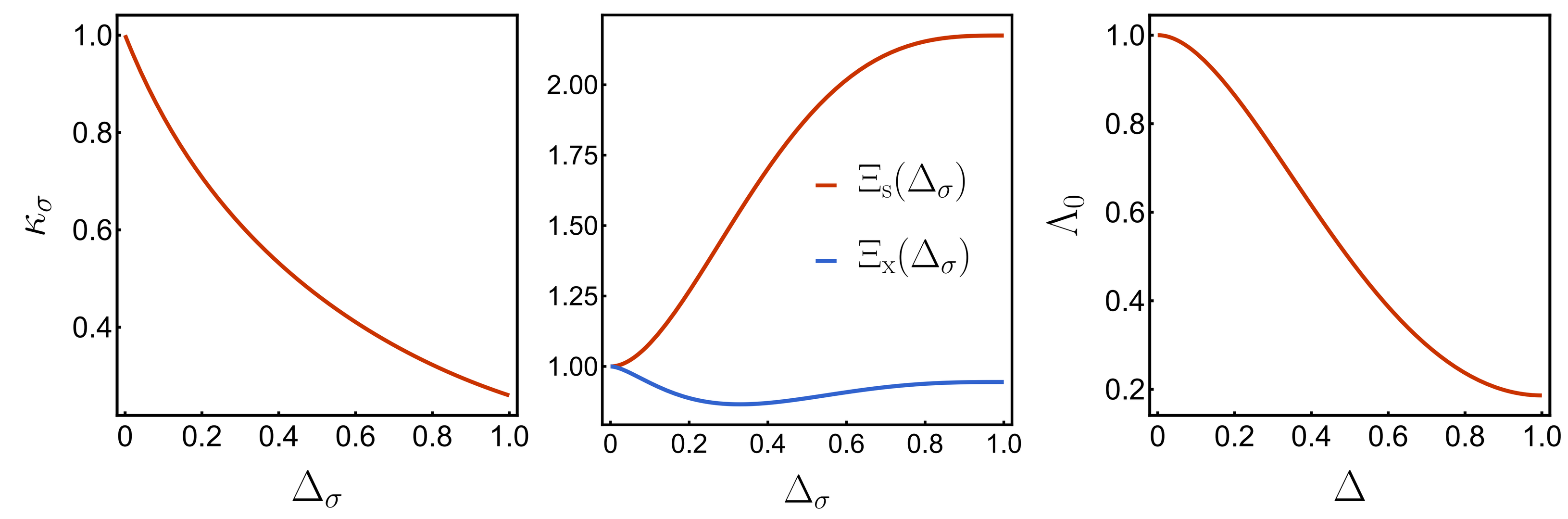
$$t_{s\sigma}(\rho_\sigma,\Delta_\sigma) = \frac{1}{\rho_\sigma}\int_0^\infty f_k \frac{k^2}{2}\frac{k^2}{2\pi^2}\,\mathrm{d}k = \Xi_s(\Delta_\sigma) C_F \rho_\sigma^{2/3}$$

$$\underbrace{\Xi_s(\Delta_\sigma)}_{\text{gap-dependent Thomas-Fermi coefficient}} = (1-\Delta_\sigma)^5 + (1+\Delta_\sigma\kappa_\sigma)^5 - 1$$

Exchange energy

$$\epsilon_{x\sigma}(\rho_\sigma,\Delta_\sigma) = \frac{1}{2}\iint \frac{\rho_x(\boldsymbol{r}_1,\boldsymbol{r}_2)}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\,\mathrm{d}\boldsymbol{r}_1\,\mathrm{d}\boldsymbol{r}_2 = \Xi_x(\Delta_\sigma) C_x \rho_\sigma^{1/3}$$

$$\begin{aligned} \underbrace{\Xi_x(\Delta_\sigma)}_{\text{gap-dependent Dirac coefficient}} &= (1-\Delta_\sigma)^4 + 4\Delta_\sigma\kappa_\sigma(1+\Delta_\sigma^2\kappa_\sigma^2) + 8\Delta_\sigma^2\kappa^2\ln 2 - \Delta_\sigma^4\kappa_\sigma^4 \\ &+ 2\Delta_\sigma^2\kappa^2\left[\left(1-\frac{\Delta_\sigma\kappa_\sigma}{2}\right)^2 \ln\left(1-\frac{\Delta_\sigma\kappa_\sigma}{2}\right) + 2\left(1-\frac{\Delta_\sigma^2\kappa_\sigma^2}{4}\right)\ln\left(\frac{\Delta_\sigma\kappa_\sigma}{2}\right)\right. \\ &+ \left.\left(1+\frac{\Delta_\sigma\kappa_\sigma}{2}\right)^2 \ln\left(1+\frac{\Delta_\sigma\kappa_\sigma}{2}\right)\right] \end{aligned}$$



Correlation Energy of Excited-State UEGs

Infrared divergence in the high-density limit

$$\epsilon^{(2)} = \underbrace{\epsilon^{(2d)}}_{\text{diverge logarithmically as } \lambda_0 \ln r_s} + \underbrace{\epsilon^{(2x)}}_{\text{finite}}$$

$$\epsilon^{(2d)} = -\frac{3}{16\pi^5}\int \frac{\mathrm{d}\boldsymbol{k}}{k^4}\int \mathrm{d}\boldsymbol{q}\int \frac{\mathrm{d}\boldsymbol{p}}{\boldsymbol{k}\cdot(\boldsymbol{p}-\boldsymbol{q}+\boldsymbol{k})}$$

$$\int \mathrm{d}\boldsymbol{q}\int \frac{\mathrm{d}\boldsymbol{p}}{\boldsymbol{k}\cdot(\boldsymbol{p}-\boldsymbol{q}+\boldsymbol{k})} \approx (2\pi)^2\int_0^1 \mathrm{d}x\int_0^1 \mathrm{d}y\int_{1-kx}^1 \mathrm{d}p\int_{1-ky}^1 \frac{\mathrm{d}q}{k(x+y)}$$

$$\epsilon^{(2d)} \approx -\frac{3}{16\pi^5}\int_{\sqrt{r_s}}^1 \frac{4\pi k^2\,\mathrm{d}k}{k^4}(2\pi)^2\frac{2k}{3}(1-\ln 2) \sim \frac{1-\ln 2}{\pi^2}\ln r_s$$

Direct component for excited-state UEGs

$$\epsilon^{(2d)}(\Delta) \sim \underbrace{\lambda_0(\Delta)}_{\Delta\text{-dependent direct component}}\ln r_s$$

$$\boxed{\lambda_0(\Delta) = \Lambda_0(\Delta)\lambda_0 = \frac{1}{\pi^2}\sum_{k=1}^6 \lambda_0^{(k)}}$$

with

$$\lambda_0^{(1)} = (1-\Delta)^3 F(1,1) \qquad \lambda_0^{(2)} = F(1,1)$$
$$\lambda_0^{(3)} = (1+\kappa\Delta)^3 F(1,1) \qquad \lambda_0^{(4)} = -2F(1-\Delta,1)$$
$$\lambda_0^{(5)} = -2F(1,1+\kappa\Delta) \qquad \lambda_0^{(6)} = 2F(1-\Delta,1+\kappa\Delta)$$

and

$$F(\alpha,\beta) = \alpha^2\beta + \alpha\beta^2 + \alpha^3\ln\alpha + \beta^3\ln\beta - (\alpha^3+\beta^3)\ln(\alpha+\beta)$$

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