Quantum and semi-classical versions of the Vashishta-Singwi theory for the warm dense uniform electron gas

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Summary

The semi-classical and quantum versions of the Vashishta-Singwi scheme (VS/qVS) employ the same generalized Singwi-Tosi-Land-Sjölander (STLS) ansatz [1], but impose the closure on the classical [2] and quantum BBGKY hierachy [3], respectively. As a consequence, the VS and qVS schemes feature a static and dynamic local field correction (LFC), respectively. Fully self-consistent solutions of the finite temperature or ground state qVS scheme have never been reported in the literature. We developed a robust numerical scheme that solves the qVS scheme for the warm dense uniform electron gas (UEG) [4]. Systematic comparison with near-exact static results obtained by the effective static approximation (ESA) [5] and with results of the STLS, qSTLS and VS schemes, revealed the high structural accuracy of the qVS scheme in the entire WDM regime. The STLS scheme still performs better thermodynamically, benefiting from a favorable cancellation of errors.

Theory

A rigorous description of the finite temperature UEG is essential for the understanding of warm dense matter [6]. The self-consistent dielectric formalism is one of the most accurate and versatile microscopic frameworks for the description of the warm dense UEG [6]. It combines the exact Matsubara summation for the static structure factor (SSF) from linear response theory and the exact density response function expression from the polarization potential approach with an approximate closure for the LFC as a functional of the SSF. **The STLS scheme** [1] is the prototypical dielectric scheme that allowed the inclusion of correlations beyond the ubiquitous random phase approximation with the STLS ansatz being:

$$f_2(\mathbf{r},\mathbf{p},\mathbf{r}',\mathbf{p}',t)=f(\mathbf{r},\mathbf{p},t)f(\mathbf{r}',\mathbf{p}',t)g(\mathbf{r}-\mathbf{r}')$$

The VS scheme [2] is based on the density expansion of a generalized STLS closure that is imposed on the classical BBGKY hierarchy. The numerical solution of the VS scheme for the warm dense UEG was recently revisited [7], correcting for an earlier thermodynamic error [8]. The **qVS scheme** emerges by closing the first member of the quantum BBGKY hierarchy (in the Wigner representation) :

$$\left\{\frac{\partial}{\partial t}+\mathbf{v}\cdot\frac{\partial}{\partial\mathbf{r}}\right\}f(\mathbf{r},\mathbf{p},t)=-\frac{1}{i\hbar}\int\frac{d^3\lambda d^3\bar{p}}{(2\pi)^3}\exp\left[i(\mathbf{p}-\bar{\mathbf{p}})\cdot\lambda\right]\left[U_{\mathrm{ext}}\left(\mathbf{r}+\frac{\hbar}{2}\lambda,t\right)-U_{\mathrm{ext}}\left(\mathbf{r}-\frac{\hbar}{2}\lambda,t\right)\right]f(\mathbf{r},\bar{\mathbf{p}},t)$$
$$-\frac{1}{i\hbar}\int\frac{d^3\lambda d^3\bar{p}}{(2\pi)^3}d^3r'd^3p'\exp\left[i(\mathbf{p}-\bar{\mathbf{p}})\cdot\lambda\right]\left[U\left(\mathbf{r}-\mathbf{r}'+\frac{\hbar}{2}\lambda\right)-U\left(\mathbf{r}-\mathbf{r}'-\frac{\hbar}{2}\lambda\right)\right]f_2(\mathbf{r},\bar{\mathbf{p}},\mathbf{r}',\mathbf{p}',t)$$

with the VS ansatz :

$$f_2(\mathbf{r},\mathbf{p},\mathbf{r}',\mathbf{p}',t)=f(\mathbf{r},\mathbf{p},t)f(\mathbf{r}',\mathbf{p}',t)\{g(\mathbf{r}-\mathbf{r}')+\alpha[\delta n(\mathbf{r},t)+\delta n(\mathbf{r}',t)][\partial g(\mathbf{r}-\mathbf{r}')/\partial n]\}$$

The compressibilty sum rule can be enforced through the free parameter $\alpha\equiv\alpha(n,T)$

$$\lim_{k\to 0}\frac{G(k,0)}{k^2}=-\frac{1}{4\pi e^2}\left[\frac{\partial^2}{\partial n^2}(nf_{xc})\right]$$

The following compact equation is derived for the qVS self-consistency parameter:

$$\alpha(r_s,\Theta)=\frac{Q(r_s,\Theta)-\left(\frac{2}{3}\Theta^2\frac{\partial^2}{\partial\Theta^2}+\frac{1}{6}r_s^2\frac{\partial^2}{\partial r_s^2}+\frac{2}{3}\Theta r_s\frac{\partial^2}{\partial\Theta\partial r_s}-\frac{1}{3}\Theta\frac{\partial}{\partial\Theta}-\frac{1}{3}r_s\frac{\partial}{\partial r_s}\right)\tilde{f}_{xc}(r_s,\Theta)}{\left(1+\frac{2}{3}\Theta\frac{\partial}{\partial\Theta}+\frac{1}{3}r_s\frac{\partial}{\partial r_s}\right)Q(r_s,\Theta)}.$$

$$Q(r_s,\Theta)=\frac{12}{\pi\lambda r_s}\frac{\int_0^\infty w\left[S(w)-1\right]dw\int_0^\infty\frac{qdq}{\exp\left(\frac{q^2}{\Theta}-\bar{\mu}\right)+1}\frac{q}{w^3}\left[\frac{q}{w}\ln\left|\frac{w+2q}{w-2q}\right|-1\right]}{\int_0^\infty\frac{dy}{\exp\left(\frac{y^2}{\Theta}-\bar{\mu}\right)+1}}.$$

Numerical algorithm

Step 1: Compute the chemical potential.

$$\int_0^\infty\frac{\sqrt{z}dz}{\exp(z-\bar{\mu})+1}=\frac{2}{3}\Theta^{-3/2}.$$

Step 2: Compute the normalized ideal density response.

$$\Phi(x,l)=\frac{1}{2x}\int_0^\infty dy\frac{y}{\exp(\frac{y^2}{\Theta}-\bar{\mu})+1}\ln\left|\frac{(x^2+2xy)^2+(2\pi l\Theta)^2}{(x^2-2xy)^2+(2\pi l\Theta)^2}\right|,$$

$$\Phi(x,0)=\frac{1}{\Theta x}\int_0^\infty dy\left[\left(y^2-\frac{x^2}{4}\right)\ln\left|\frac{2y+x}{2y-x}\right|+xy\right]\frac{y\cdot\exp\left(\frac{y^2}{\Theta}-\bar{\mu}\right)}{\left[\exp\left(\frac{y^2}{\Theta}-\bar{\mu}\right)+1\right]^2}.$$

Step 3: As initial guess use the STLS SSF and $0.1\leq\alpha_{num}\leq 1$ to compute the auxiliary density response Ψ_{qVS} for the 9 state points shown in Fig. 1.

$$\Psi_{qSTLS}(x,l)=-\frac{3}{8}\int_0^\infty w\left[S(w)-1\right]dw\int_0^\infty\frac{qdq}{\exp\left(\frac{q^2}{\Theta}-\bar{\mu}\right)+1}\int_{x^2-xw}^{x^2+xw}\frac{dt}{2t+w^2-x^2}\ln\left[\frac{(2xq+t)^2+(2\pi l\Theta)^2}{(2xq-t)^2+(2\pi l\Theta)^2}\right],$$

$$\Psi_{qSTLS}(x,0)=-\frac{3}{4\Theta}\int_0^\infty w\left[S(w)-1\right]dw\int_0^\infty\frac{q\exp\left(\frac{q^2}{\Theta}-\bar{\mu}\right)dq}{\left[\exp\left(\frac{q^2}{\Theta}-\bar{\mu}\right)+1\right]^2}\int_{x^2-xw}^{x^2+xw}\frac{dt}{2t+w^2-x^2}\left[\left(q^2-\frac{t^2}{4x^2}\right)\ln\left|\frac{t+2xq}{t-2xq}\right|+\frac{q}{x}t\right],$$

$$\Psi_{qVS}(x,l)=\left[1+\alpha_{num}\left(\frac{1}{3}-\frac{2}{3}\Theta\frac{\partial}{\partial\Theta}-\frac{1}{3}r_s\frac{\partial}{\partial r_s}-\frac{1}{3}x\frac{\partial}{\partial x}\right)\right]\Psi_{qSTLS}(x,l).$$

Step 4: Compute the SSF for all 9 state points.

$$S(x)=\frac{3}{2}\Theta\sum_{l=-\infty}^{+\infty}\frac{\Phi(x,l)}{1+\frac{4}{\pi}\lambda r_s\frac{1}{x^2}[\Phi(x,l)-\Psi_{\mathrm{qVS}}(x,l)]}.$$

Step 5: Repeat steps 3,4 (inner loop) until SSF convergence is reached on the central point.

Step 6: Compute $\tilde{f}_{xc}(r_s,\Theta)$ and $Q(r_s,\Theta)$ on the 9 state points in order to obtain $\alpha(r_s,\Theta)$.

Step 7: Repeat inner loop until convergence is reached between $\alpha(r_s,\Theta)$ and α_{num} (outer loop).

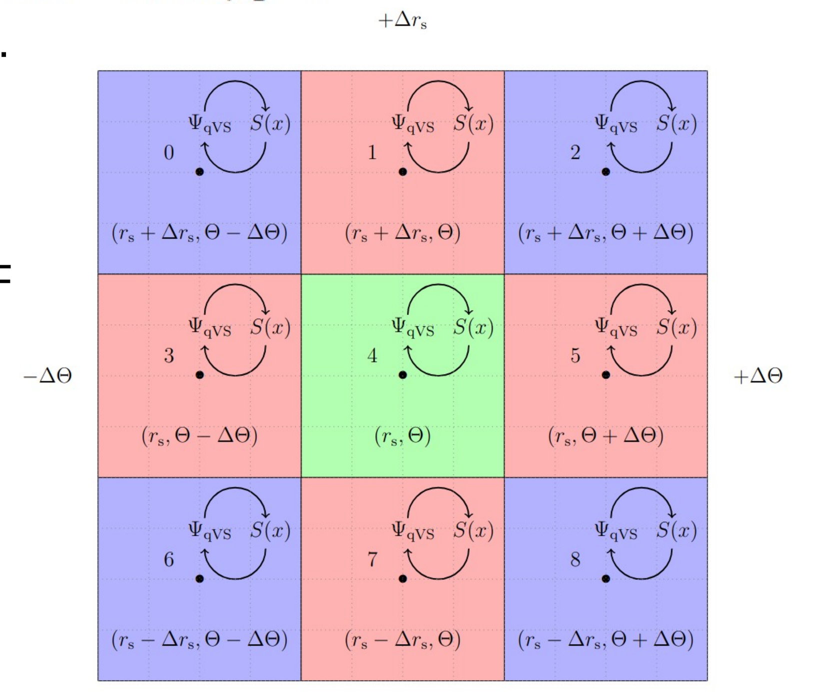

FIG. 1: 2D grid for the finite difference approximation of the state point derivatives.

Static structure factor

Systematic comparison with the near-exact results of the ESA scheme and the results of the STLS, qSTLS and VS schemes, reveals a structural superiority of the qVS over the STLS, qSTLS and VS schemes in the entire WDM regime.

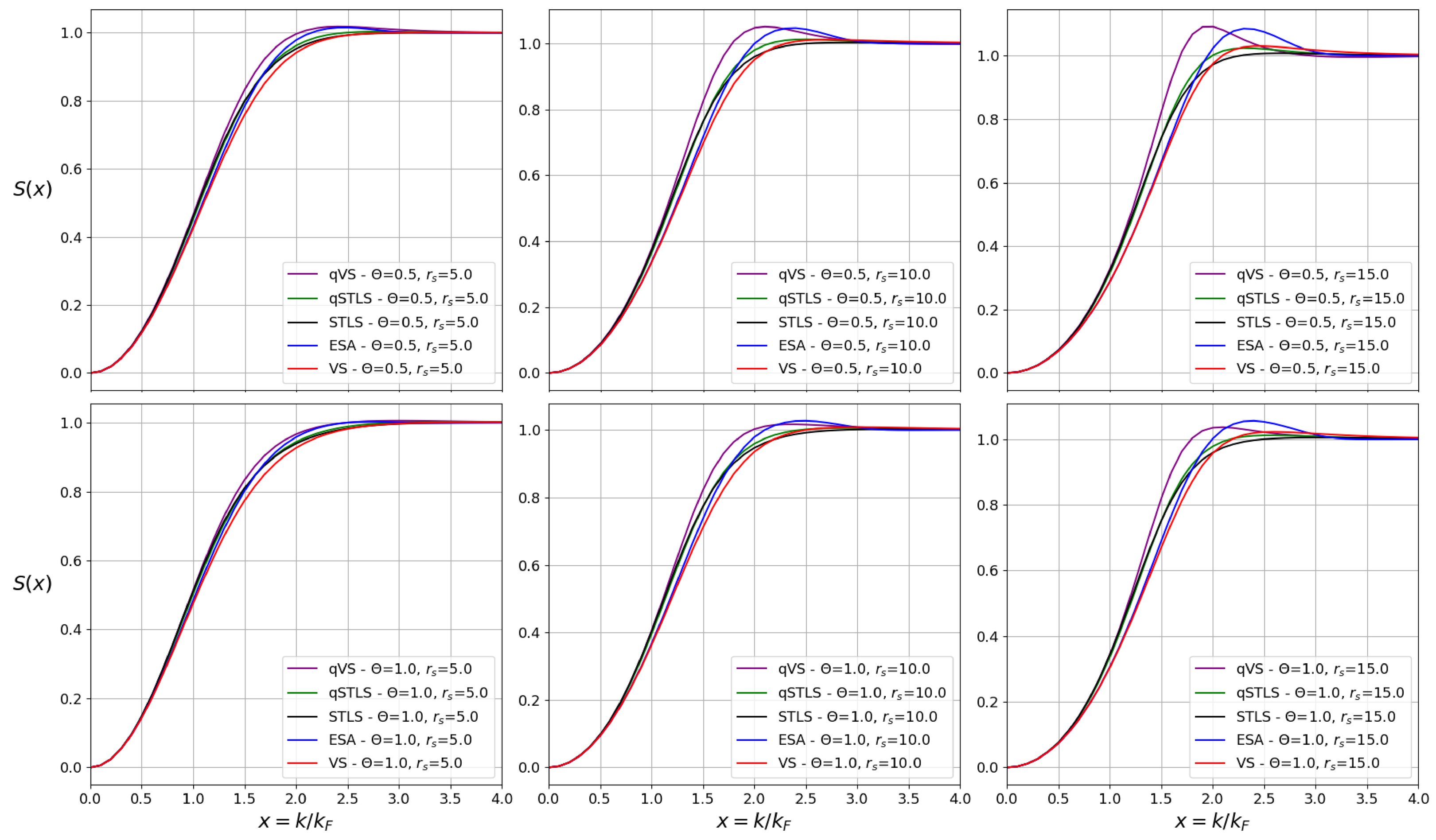

FIG. 2: The static structure factor of the paramagnetic uniform electron fluid in the warm dense matter regime, as predicted by the qVS scheme (purple), the STLS scheme (black), the quasi-exact ESA scheme (blue), the VS (red) and qSTLS (green). Results for $\Theta=0.5$ (top), $\Theta=1.0$ (bottom) and for $r_s=5$ (left), $r_s=10$ (center), $r_s=15$ (right).

Overall, the qVS SSF seems to have a well-pronounced maximum, albeit it being slightly over-pronounced closer to the ground state and under-pronounced once the degeneracy parameter is increased. Additionally, its position is slightly shifted from the expected ESA in the whole WDM regime.

Self-consistency parameter

The general observed trend is that the free parameter for any Θ is a monotonically increasing function of the quantum coupling parameter that rises abruptly until it reaches an extended plateau. For any r_s the free parameter is a monotonically decreasing function of the degeneracy parameter up to $\Theta\sim 4$,

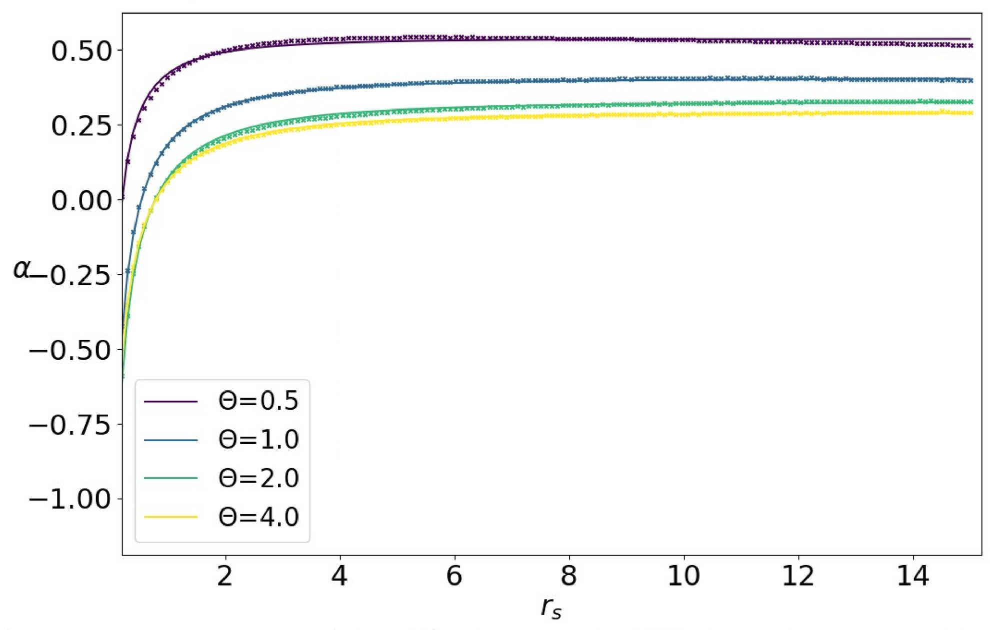

FIG. 3: (Main) Dependence of the self-consistency parameter α of the qVS scheme on the UEF thermodynamic variables. Numerical data (symbols) and analytic fits (solid lines) for $r_s=0.5-15$ and $\Theta=0.5$ (purple), $\Theta=1.0$ (gray), $\Theta=2.0$ (green), $\Theta=4.0$ (yellow).

Exchange-Correlation energy

Owing to a favourable cancellation of errors in the integration of the SSF, the STLS scheme still remains thermodynamically superior in comparison to qVS especially closer to the ground state where the degeneracy parameter is below unity.

However, as the degeneracy parameter is increased, we observe a gradual reduction in the qVS deviation from the GDSMFB parametrization [9].

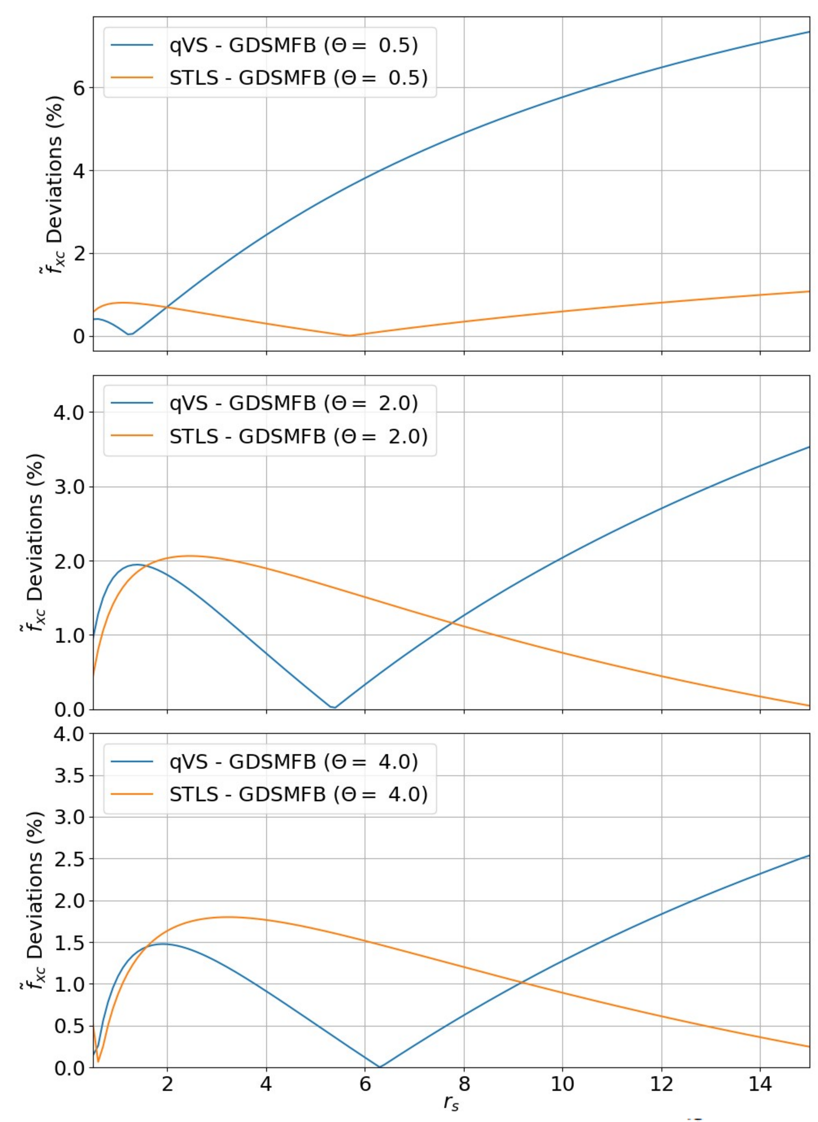

FIG. 4: The absolute relative deviations of the qVS $\tilde{f}_{xc}$ predictions (blue) and the STLS $\tilde{f}_{xc}$ predictions (orange) from the very accurate $\tilde{f}_{xc}$ value of the GDSMFB parametrization as a function of r_s for $\Theta=0.5$ (top), $\Theta=2.0$ (centre) and $\Theta=4.0$ (bottom). In the case of $\Theta=0.5$, the abrupt monotonicity changes that appear for both STLS and qVS correspond to the switch of the sign of the difference.

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