Thermal DFT (2nd Half)

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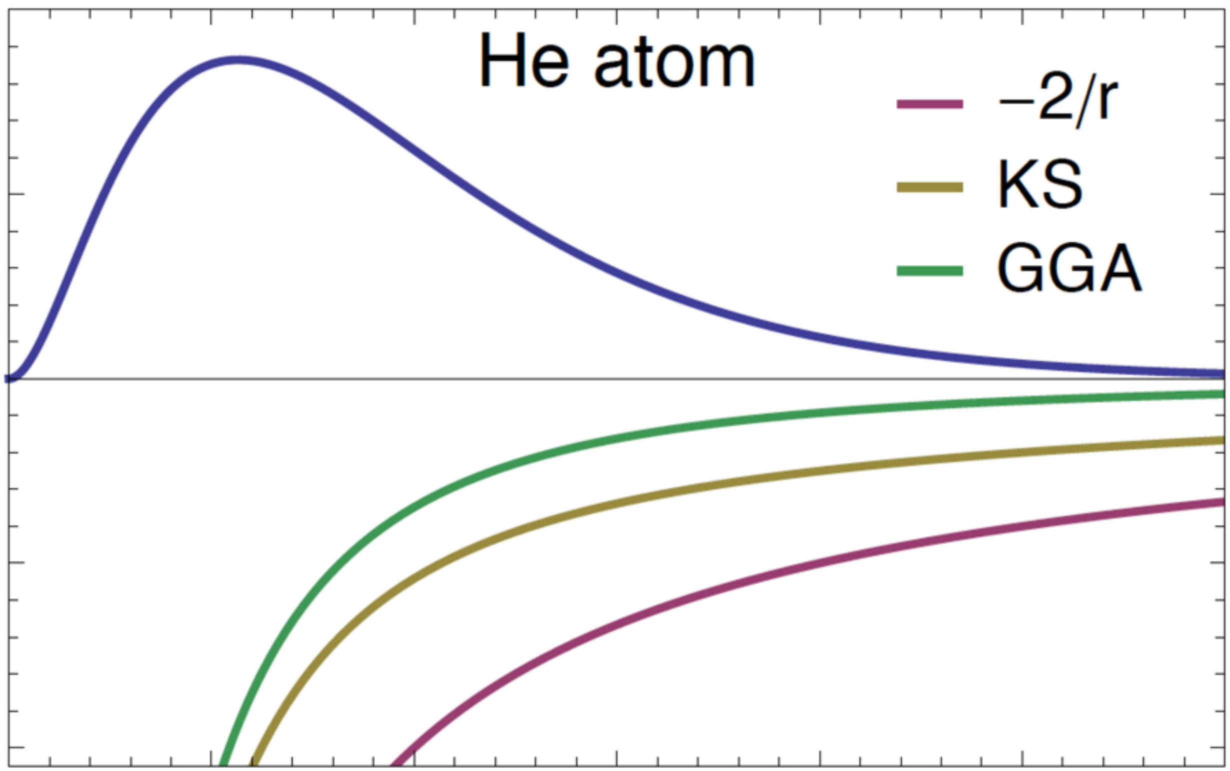
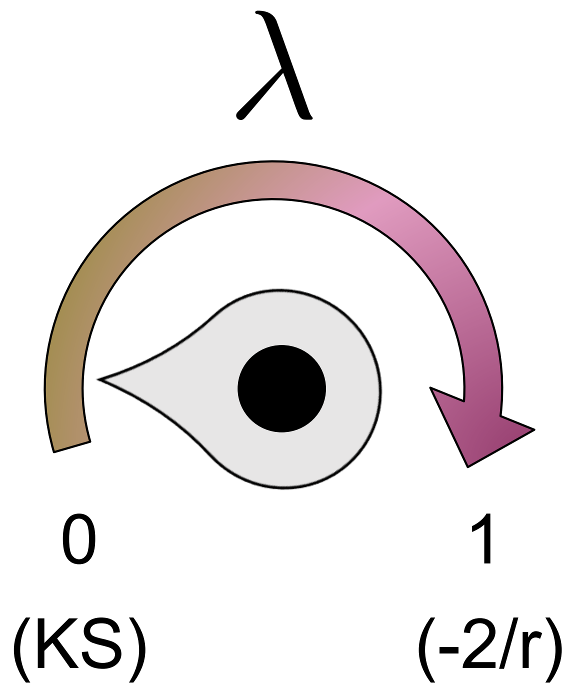
Adiabatic Connection Formula

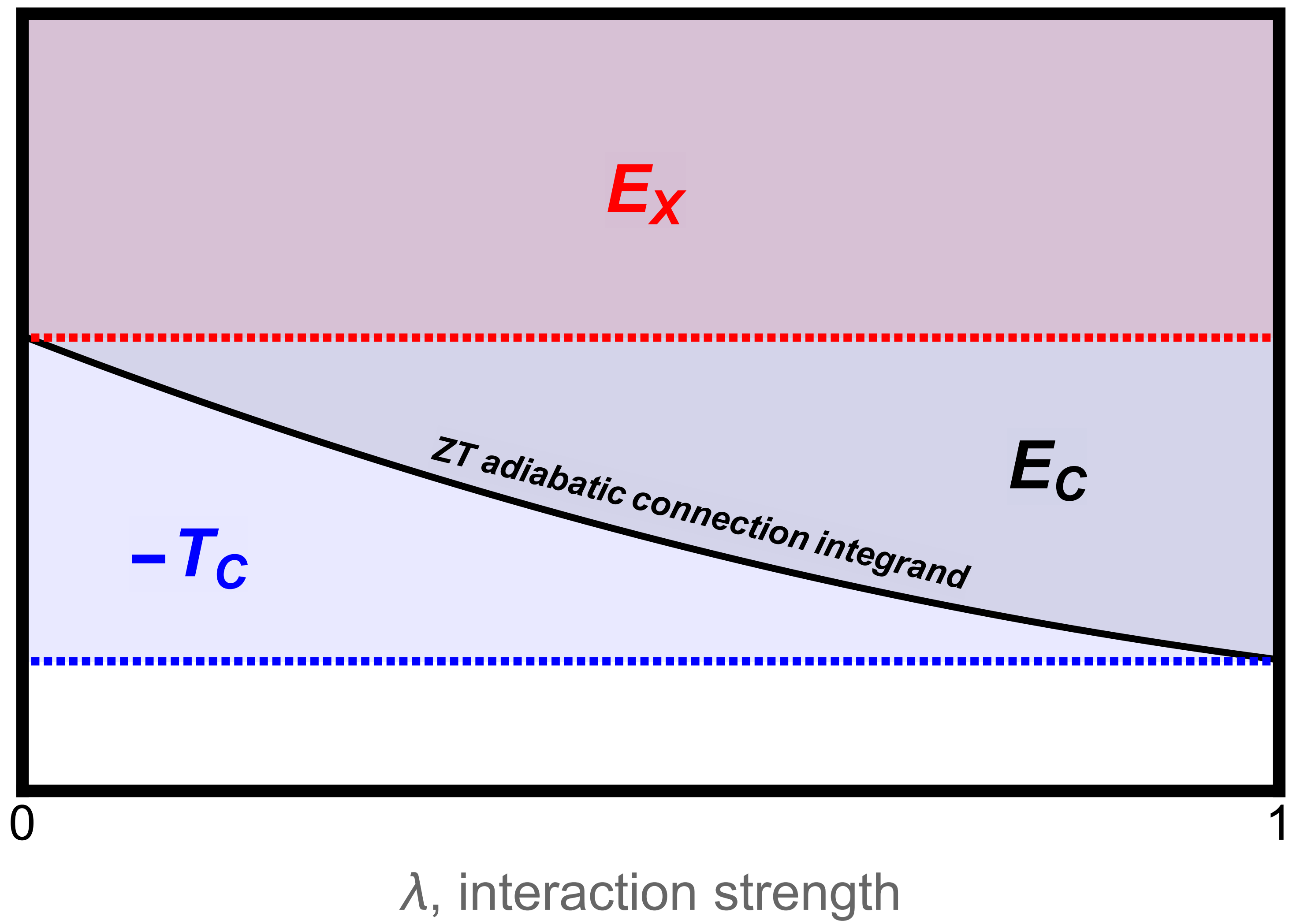
$$E_{xc}[n] = \int_0^1 d\lambda \frac{U_{xc}^{\lambda}[n]}{\lambda}$$





APJ et al., Ann. Rev. Phys. Chem **66** (2015),

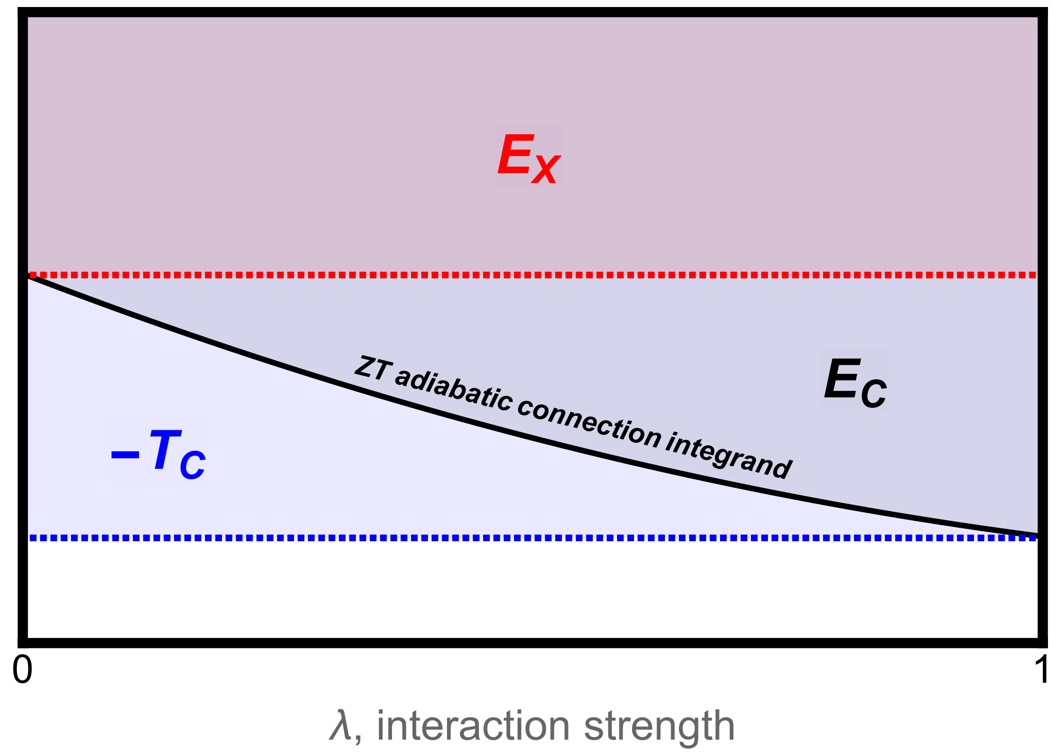
Cartoon: Adiabatic Connection



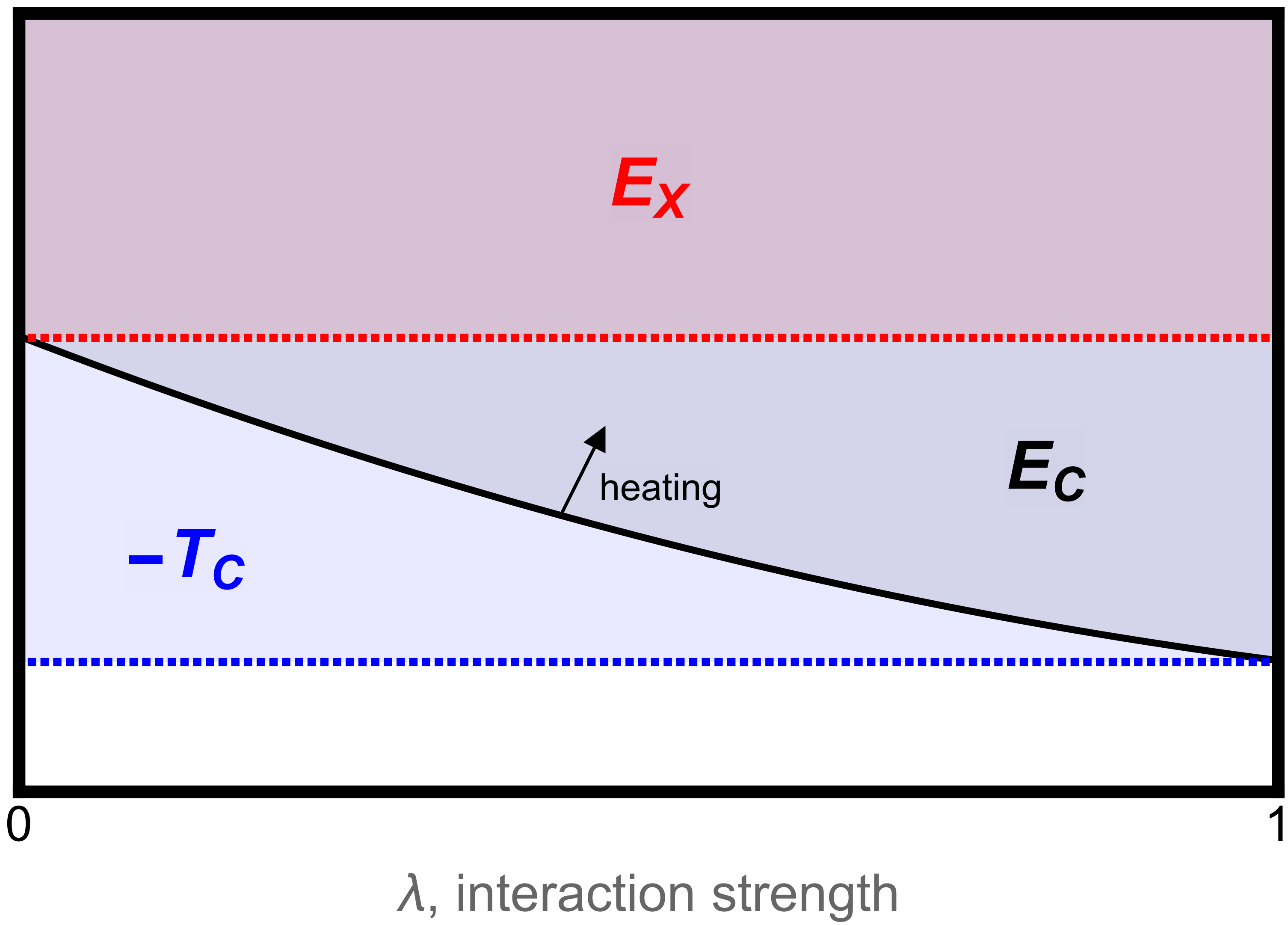
Next!

Grab some paper to draw, if you like.

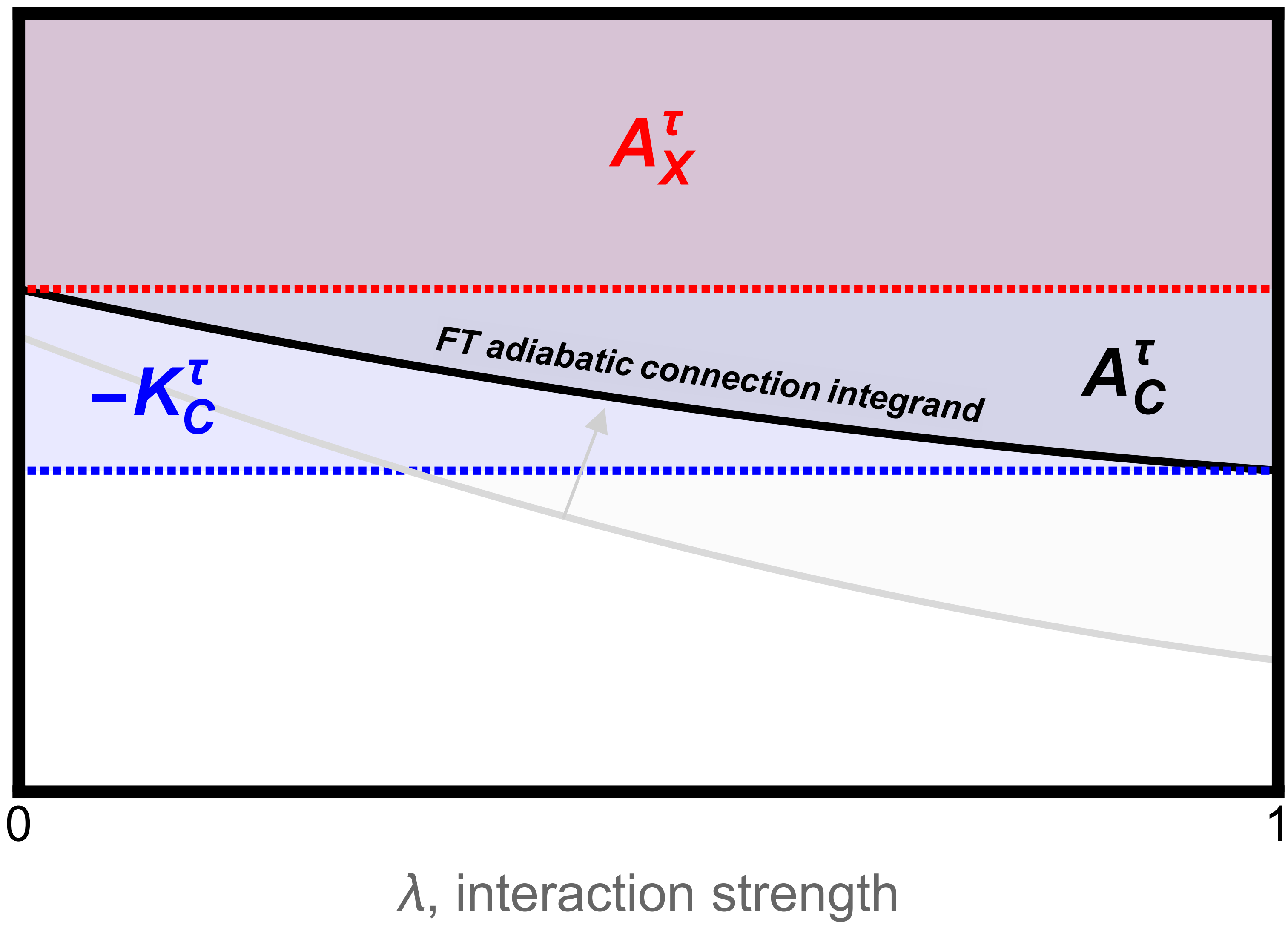
1. *What would a similar cartoon for non-zero temperatures look like?*
2. *Should the adiabatic connection curve move up or down as temperatures increase?*



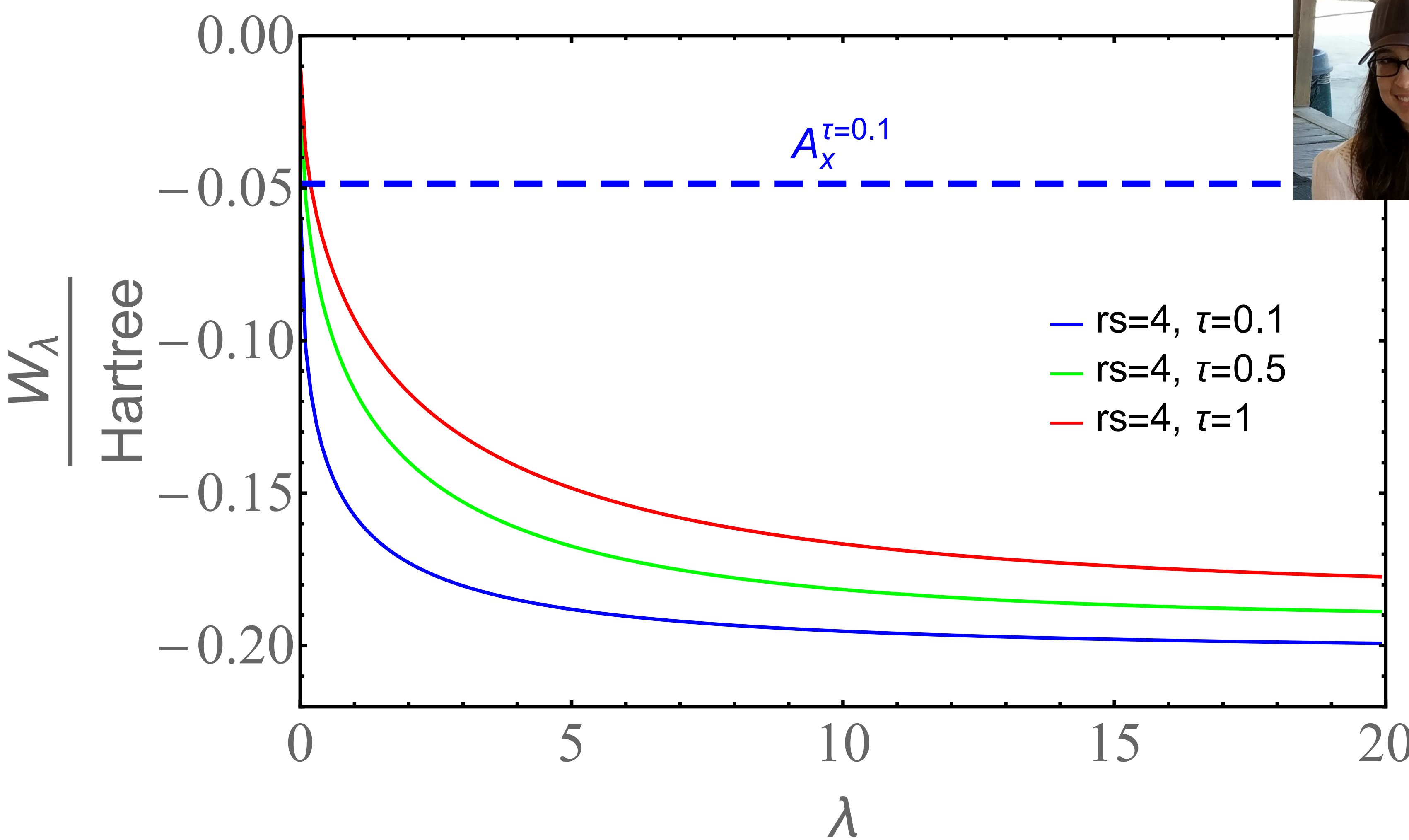
Heating



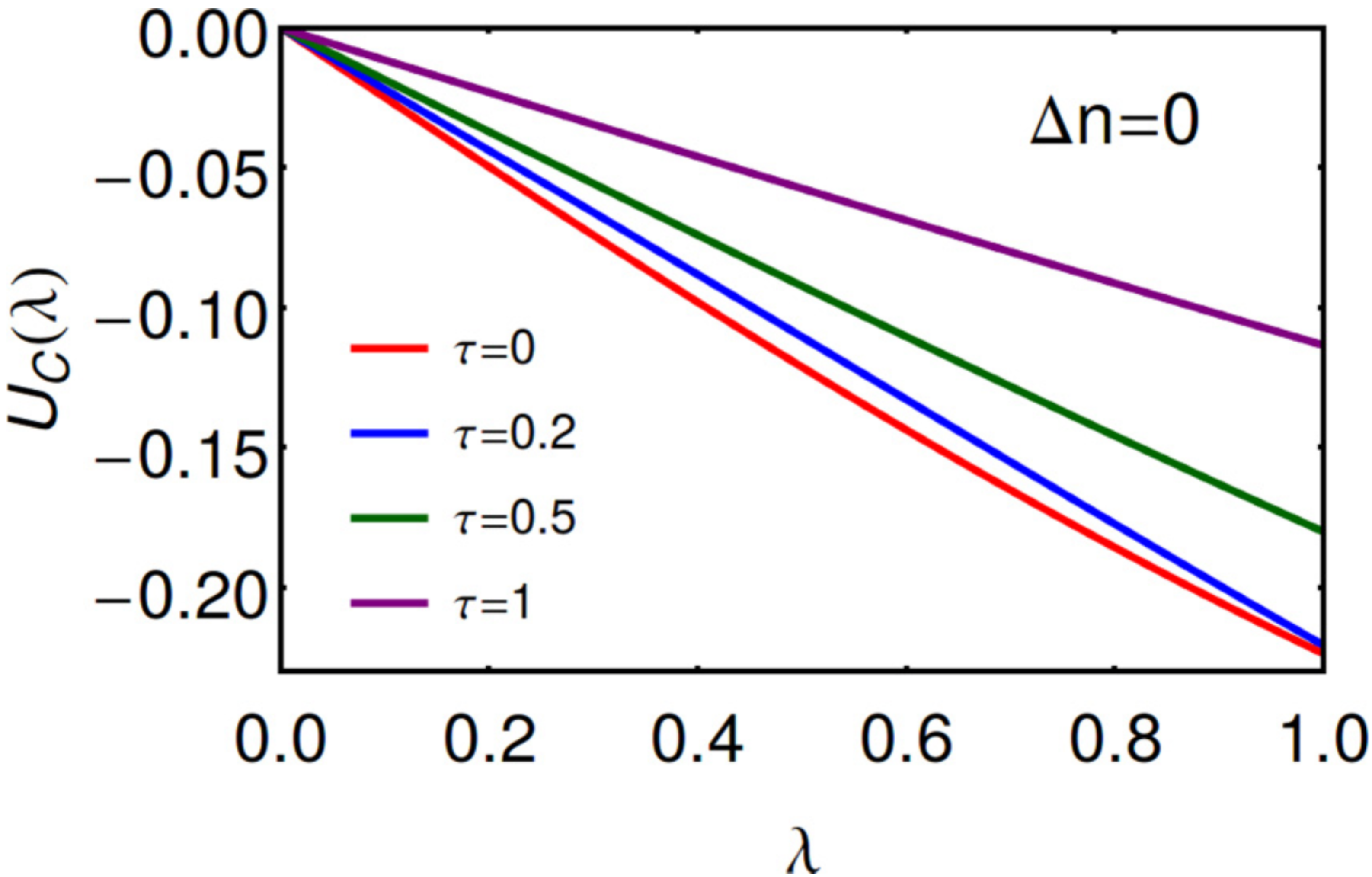
Thermal Adiabatic Connection



Uniform Gas Thermal AC

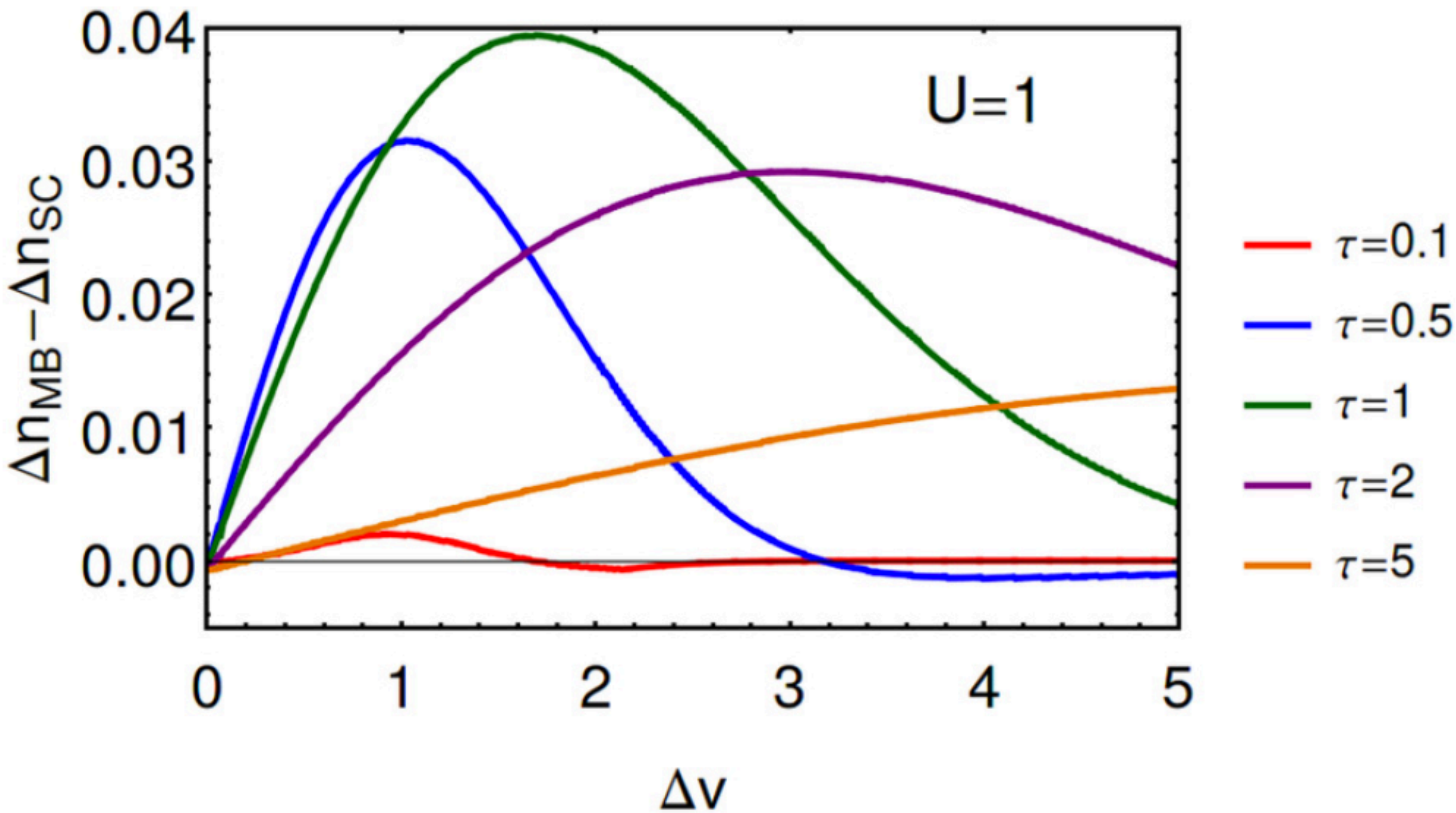


Hubbard Dimer Thermal AC



Smith, J.C., APJ, Burke, K. Phys. Rev. B, **93**, 245131 (2016).

Thermal Hubbard Dimer: ZTA



Smith, J.C., APJ, Burke, K. Phys. Rev. B, **93**, 245131 (2016).

Another One?

For discussion with your neighbors:

- *The thermal asymmetric Hubbard dimer shows an intermediate-temperature region where the ZTA performs worse than at higher or lower temps. What are some reasons for such a spot?*

  In other words, why would temperature XC effects be less important at low temperatures, and why at high temperatures? Is it the same reason?

Correlation Relations

Correlation free energy: kentropic, potential, kinetic, entropic

$$A_{\mathrm{C}}^{\tau}[n] = K_{\mathrm{C}}^{\tau}[n] + U_{\mathrm{C}}^{\tau}[n]$$

$$K_{\mathrm{C}}^{\tau}[n] = T_{\mathrm{C}}^{\tau}[n] - \tau\, S_{\mathrm{C}}^{\tau}[n]$$

Combine with ACF to get a set of relations, such as:

$$A_{\mathrm{C}}^{\tau}[n] = -\int_0^1 \frac{d\lambda}{\lambda^2}\, K_{\mathrm{C}}^{\tau,\lambda}[n]$$

APJ and Burke, PRB, 93, 205140 (2016).

Coupling Constant → Temperature

Combine finite-temperature ACF

$$A_{\rm C}^{\tau}[n] = \int_0^1 \frac{d\lambda}{\lambda}\, U_{\rm C}^{\tau,\lambda}[n]$$

with coupling constant-coordinate-temperature scaling.

$$A_{\rm XC}^{\tau,\lambda}[n] = \lambda^2\, A_{\rm XC}^{\tau/\lambda^2}[n_{1/\lambda}]$$

Change of variables yields thermal connection formula:

$$A_{\rm XC}^{\tau}[n] = \frac{\tau}{2} \lim_{\tau''\to\infty} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2}\, U_{\rm XC}^{\tau'}[n_{\sqrt{\tau'/\tau}}]$$

APJ and Burke, PRB, 93, 205140 (2016).

Thermal Connection Formula

$$A_{\rm XC}^{\tau}[n] = \frac{\tau}{2} \lim_{\tau'' \to \infty} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2} U_{\rm XC}^{\tau'}[n_{\sqrt{\tau'/\tau}}]$$

- Relates exact XC free energy to high temperature, high density limit
- Need knowledge of XC potential energy at scaled densities, ***not*** at scaled interaction strengths
- Reduces to plasma physics coupling-constant relation for uniform systems
- Generalization of plasma physics formula to density functionals and inhomogeneous systems

Linear Response: Thermal Ensembles

Like van Leeuwen's 2001 invertibility proof, but for thermal ensembles. Hinges on showing positivity of each factor in this expression:

$$m^{\tau}(s) = -2 \sum_{i=0}^{\infty} \sum_{j=i+1}^{\infty} \frac{(\mathtt{w}_i - \mathtt{w}_j)\omega_{ji}}{s^2 + \omega_{ji}^2} \mid \Delta V_{ij}^{\tau}(s) \mid^2$$

<u>KEY POINT</u> Laplace-transformable potentials, i.e., switch-on processes

→ relaxes BC, analyticity requirements

APJ, Grabowski, and Burke, PRL 116, 233001 (2016)

An "Application"

Using finite-temperature fluctuation-dissipation theorem for the correlation free energy in terms of the thermal density-density response function:

$$A_{\rm C}^{\tau}[n] = \lim_{\tau''\to\infty} \frac{\tau}{2} \int_{\tau}^{\tau''} \frac{d\tau'}{\tau'^2} \int d\mathbf{r} \int d\mathbf{r}' \int \frac{d\omega}{2\pi} \coth\left(\frac{\omega}{2\tau}\right) \frac{\Im \Delta\chi^{\tau'}[n_\gamma](\mathbf{r},\mathbf{r}',\omega)}{|\mathbf{r}-\mathbf{r}'|}$$

Useful for computation and theory:

•Generates ***new*** XC approximations for FT DFT
•Provides link between finite-temperature and infinite-temperature limit

APJ, Grabowski, and Burke, PRL 116, 233001 (2016)

Static XC Approximations via TDDFT

Exact expression, as long as exact thermal kernel is used:

$$(\chi_S^\tau)^{-1}(12) = (\chi^\tau)^{-1}(12) + f_H(12) + f_{XC}^\tau(12)$$

Approximations to thermal XC kernel:

- $f_{XC}^\tau(12)$ = 0 → thermal RPA

- $$f_{XC}^{\tau,\mathrm{thALDA}}[n](\mathbf{r},\mathbf{r}',\omega) = \left.\frac{d^2 a_{XC}^{\tau,\mathrm{unif}}(n)}{d^2 n}\right|_{n(\mathbf{r})} \delta(\mathbf{r}-\mathbf{r}')$$

→ Approximate $A_{XC}^\tau[n]$

APJ, Grabowski, and Burke, PRL 116, 233001 (2016)

Thermal LR-TDDFT Exact Conditions

Zero-force theorem:

$$\int d^3r \int d^3r' n^\tau(\mathbf{r}) n^\tau(\mathbf{r}') f^\tau_{XC}(\mathbf{r}, \mathbf{r}', \omega) = 0$$

Tied coordinate-temperature-interaction strength-frequency scaling for response function, kernel, and potential perturbation:

$$\chi^{\tau,\lambda}[n](\mathbf{r}, \mathbf{r}', \omega) = \lambda^4 \chi^{\tau/\lambda^2}[n_{1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}', \omega/\lambda^2)$$

$$f^{\tau,\lambda}_{\mathrm{XC}}[n](\mathbf{r}, \mathbf{r}', \omega) = \lambda^2 f^{\tau/\lambda^2}_{\mathrm{XC}}[n_{1/\lambda}](\lambda\mathbf{r}, \lambda\mathbf{r}', \omega/\lambda^2)$$

$$\delta v^{\tau,\lambda}_{\mathrm{XC}}[n](\mathbf{r}, \omega) = \lambda^2 \delta v^{\tau/\lambda^2}_{\mathrm{XC}}[n_{1/\lambda}](\lambda\mathbf{r}, \omega/\lambda^2)$$

APJ, Grabowski, and Burke, PRL 116, 233001 (2016)

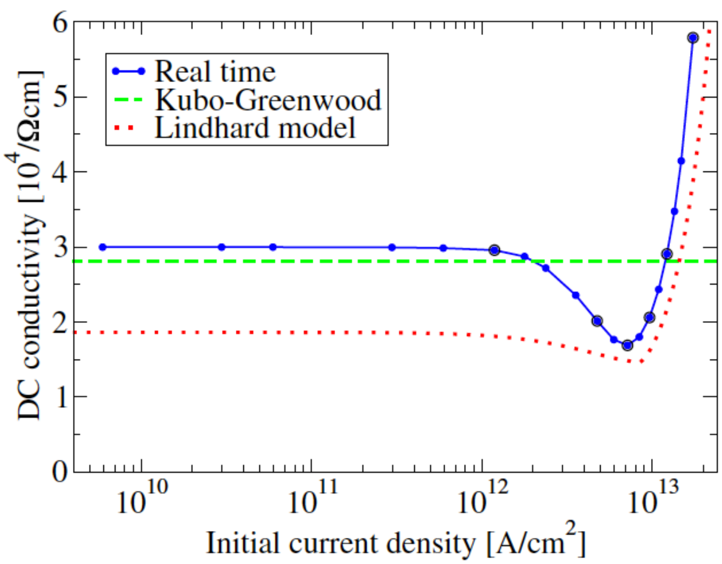
Actual Applications of Thermal TDDFT

Three of the main people working with TDDFT for thermal systems are here!

Response of WDM systems and more.
My faves:

•Andrew: X-ray Thomson scattering (diagnostic via dynamic structure factor – temperature, density structure, ionization state)

•Xavier and Alicia: Non-linear conductivities for WDM (electronic and thermal)



Baczewski et al., PRL 116, 115004 (2016). Andrade et al., Eur. Phys. J. B (2018) 91: 229

Open Questions and References

Open Questions in TDDFT for Thermal Ensembles
- Big issues: static temperatures? Non-equilibrium temperatures?
- Is lack of memory/frequency dependence more or less serious?
- How to handle energy transfer between electrons and ions?

Some of the MANY things I didn't get to today:

- **FT XC approximations (my talk Monday; work by Sjostrom, Trickey)**
- **Orbital-free approaches and semiclassics for WDM**
- **Extending strictly correlated electron methods to thermal ensembles**
- **Quantum theory of heat (Eich and Vignale)**

Literature to watch: Eich, Vignale, Baczewski, Andrade, Correa, Cangi, Sjostrom, Sagredo, Trickey, Karasiev, Desjarlais, many more…

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CfHEDS (Grant DE-NA0003866)
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