



Role of the quasi-bound and continuum states in the thermo-dynamic properties of non-ideal molecular gases at high temperature.

Classical and quantum approach.

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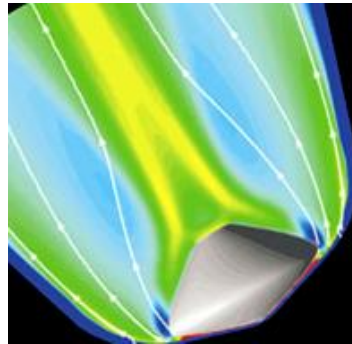
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Motivation

- **High temperature aero- and astrophysics**
- **Strong shock waves**
- **Low pressure hydrogenous plasma**



Problem

“Non-equilibrium” temperature

5000-50000 K

The conventional handbooks
(IVTAN-THERMO, JANAF)

do not **REALLY** help !!!

Particular Interest

Thermodynamic and transport properties of the entire disturbed area around the reentry hypersonic vehicles



Multi-temperature molecular partition function based on approximate separation kinds of motion

- Translation&Internal (exact)

$$Z = Z_{tr} Z_{int} \longrightarrow T_{tr} \neq T_{int}$$

$$Z = \sum_i \exp\left(-\frac{E_i}{k_B T}\right)$$

- Electronic&Rovibrational (adiabatic or BO approximation)

(it is not out question for high temperature condition)

$$Z_{int} \approx Z_{el} Z_{vib-rot} \longrightarrow T_{el} \neq T_{vib-rot}$$

$$E_{int} \approx E_{el} + E_{vib-rot}$$

- Vibrational&Rotational (harmonic oscillator-rigid rotator approximation)

$$Z_{vib-rot} \approx Z_{vib} Z_{rot} \longrightarrow T_{vib} \neq T_{rot}$$

$$E_{vib-rot} \approx E_{vib} + E_{rot}$$

Quantum method

Solution of the radial Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dR^2} + \frac{\hbar^2}{2mR^2} J(J+1) + U(R) \right] \Psi_{vJ} = E_{vJ} \Psi_{vJ}$$

with boundary conditions:

$$\begin{array}{lll} \psi(r \rightarrow 0) = 0 & \psi(r \rightarrow \infty) = 0 & \text{bound} \\ & \psi(r \rightarrow \infty) = \sin(kr + \eta_l(\varepsilon) - l\pi/2) & \text{unbound} \end{array}$$

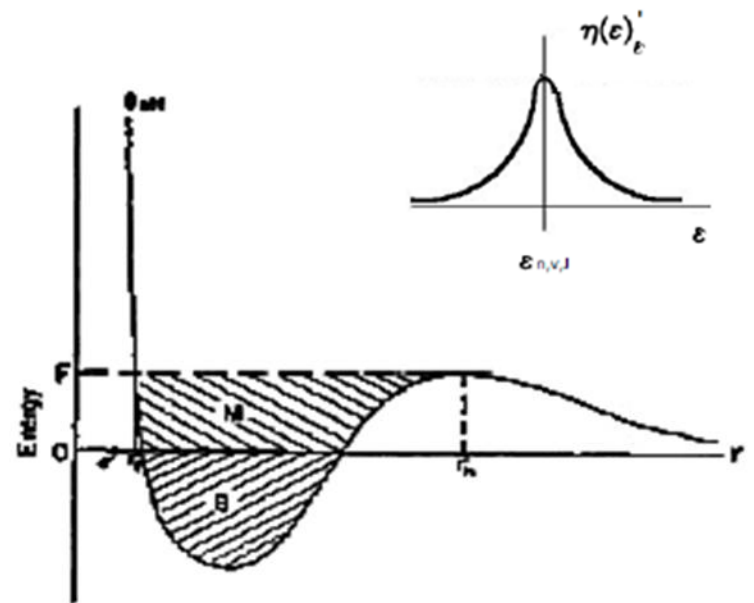


$$Z_{int} = \sum_n g_S(n) \sum_{J=0}^{\infty} (2J+1) [Z_{bound} + Z_{unbound}]$$

$$g_S(n) = (2S+1)(2 - \delta_{0,\Lambda})$$

$$Z_{bound} = \sum e^{-\frac{E_{nvJ}}{k_B T}}$$

$$Z_{unbound} = \int_0^{\infty} \rho_J(\varepsilon) e^{-\frac{\varepsilon}{k_B T}} d\varepsilon; \quad \rho_J = \frac{1}{\pi} \left(\frac{d\eta_J}{d\varepsilon} \right)$$



Role of continuum and quasi-bound states

$$Z_{int} = \sum_n g_S(n) \sum_{J=0}^{\infty} (2J+1) \left(\sum_v^{v_{max}} e^{-\frac{E_{nvJ}}{k_B T}} - 1 \right) + \frac{1}{\pi k_B T} \int_0^{\infty} \eta_J(\epsilon) e^{-\frac{\epsilon}{k_B T}} d\epsilon$$

Integration by parts + Levinson theorem: $\eta_J(\epsilon = 0) = \pi \nu_{max}$

The collision lifetime: $\tau(\epsilon) = 2\hbar \frac{\partial \eta_J}{\partial \epsilon} \ll t$

The comprehensive quantum model must take into account bound, quasi-bound and unbound states

This full form of the interacting-particle partition function is essential to a **complete** and **correct** calculation of the thermodynamic functions of the system.

Accurate thermodynamic results for high temperature require that the bound-state levels and the phase shifts both should be calculated in the same manner and to the same degree of accuracy.

Classical statistic mechanic method

$$Z^{cl}(T, n) = \frac{1}{h^n} \int e^{-\frac{H(p,q)}{k_B T}} dpdq$$

$$Z_v^{cl} = \frac{1}{\sigma \lambda} \int_0^\infty \left[1 - e^{-\frac{V(r)}{k_B T}} \right] dr$$

$$Z_{vr}^{cl} = \frac{4\pi}{\sigma \lambda^3} \int_0^\infty \left[1 - e^{-\frac{V(r)}{k_B T}} \right] r^2 dr$$

$$\lambda = 2 \sqrt{\left(\frac{\hbar^2}{2\mu} \right) \frac{\pi}{k_B T}}$$

$$Z_{vr}(T_v; T_r) \approx \frac{4\pi}{\sigma \lambda^2(T_r) \lambda(T_v)} \int_0^\infty \left[1 - e^{-\frac{V(r)}{k_B T_v}} \right] r^2 dr$$

$$Z_{vbound}^{cl} = \frac{1}{\sigma \lambda} \int_{r_{min}}^\infty e^{-\frac{V(r)}{k_B T}} \operatorname{erf} \sqrt{-\frac{V(r)}{k_B T}} dr$$

$$Z_{vrbound}^{cl} = \frac{8\sqrt{\pi}}{\sigma \lambda^3} \int_{r_{min}}^\infty \left[\frac{\sqrt{\pi}}{2} e^{-\frac{V(r)}{k_B T}} \operatorname{erf} \sqrt{-\frac{V(r)}{k_B T}} - \sqrt{-\frac{V(r)}{k_B T}} \right] r^2 dr$$

Quasi-classical correction to the classical mechanic method

$$Z_{vr}^{qc} = \left[Z_{vr}^{cl} + \left(\frac{\hbar^2}{\mu} \right) Z_{vr}^I + \left(\frac{\hbar^2}{\mu} \right) Z_{vr}^{II} \dots \right]$$

$$Z_{vr}^I(T) = \frac{4\pi}{48\pi^2\sigma(k_B T)^3} \int_0^\infty [V'(r)]^2 e^{-\frac{V(r)}{k_B T}} r^2 dr$$

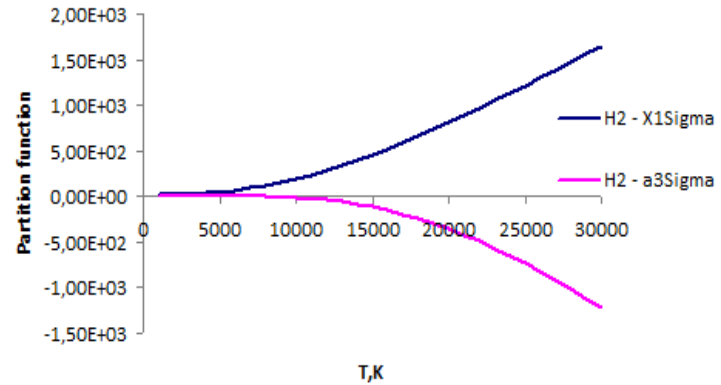
$$Z_{vr}^{II}(T) = -\frac{4\pi}{1920\sigma(\pi k_B T)^4} \int_0^\infty f(r) e^{-\frac{V(r)}{k_B T}} r^2 dr$$

$$f(r) = [V''(r)]^2 + 2\frac{V^2(r)}{r^2} + 10\frac{V^3(r)}{9k_B T r} - 5\frac{[V'(r)]^4}{36(k_B T)^2}$$

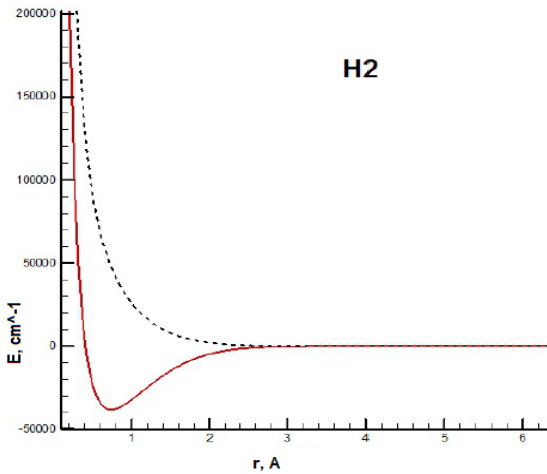
The 1-st and 2-nd derivatives of the potential are needed !

Testing implementations to hydrogen molecule

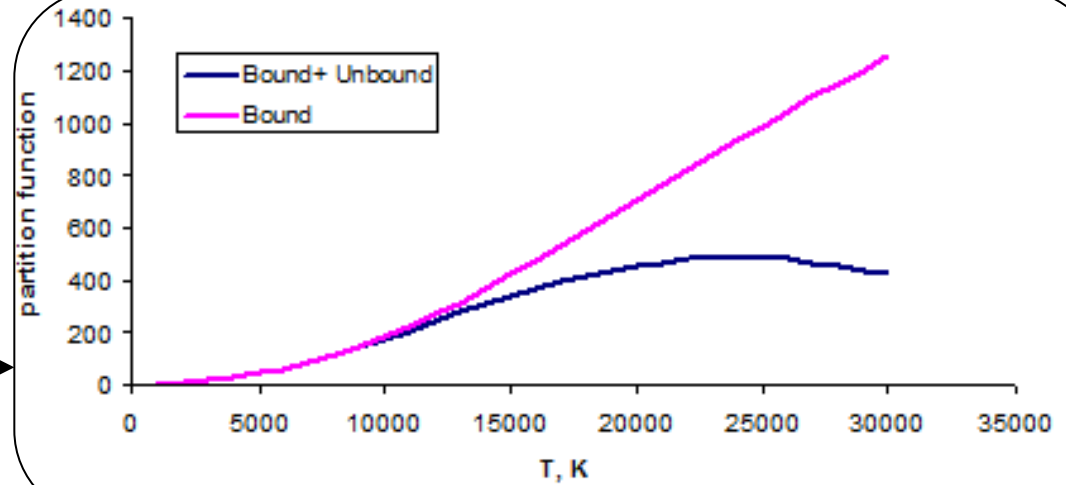
Impact of the excited repulsive state



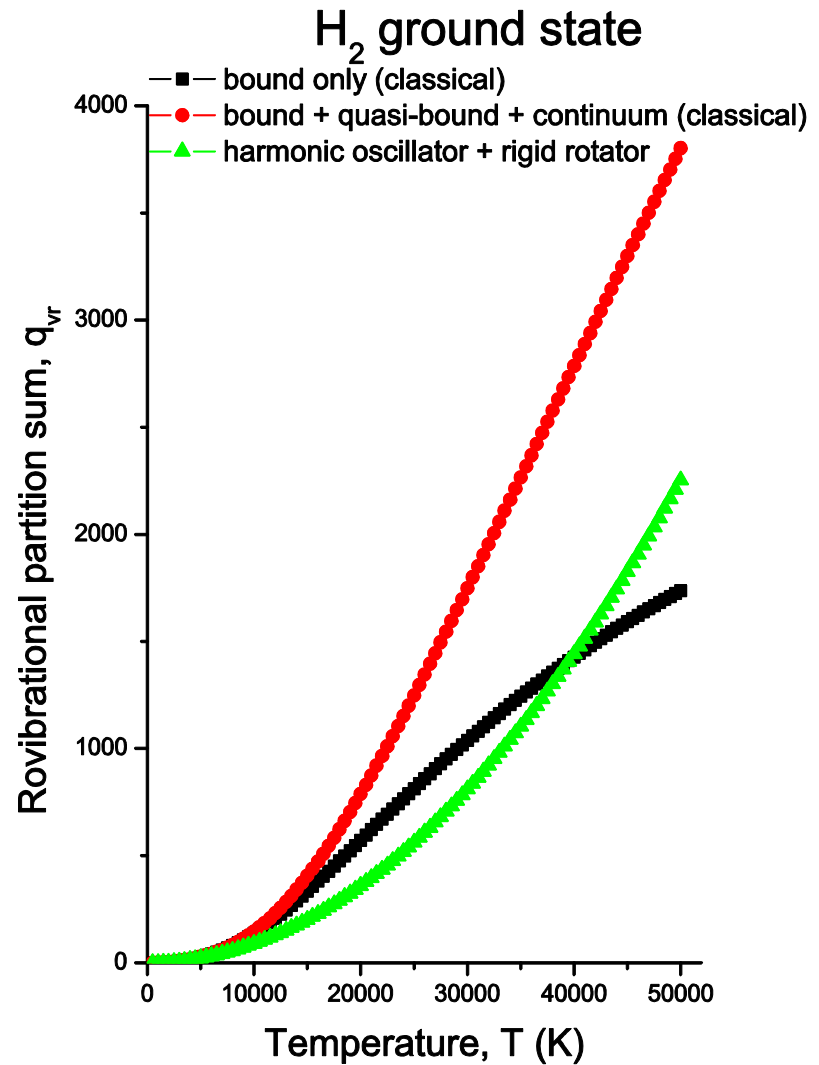
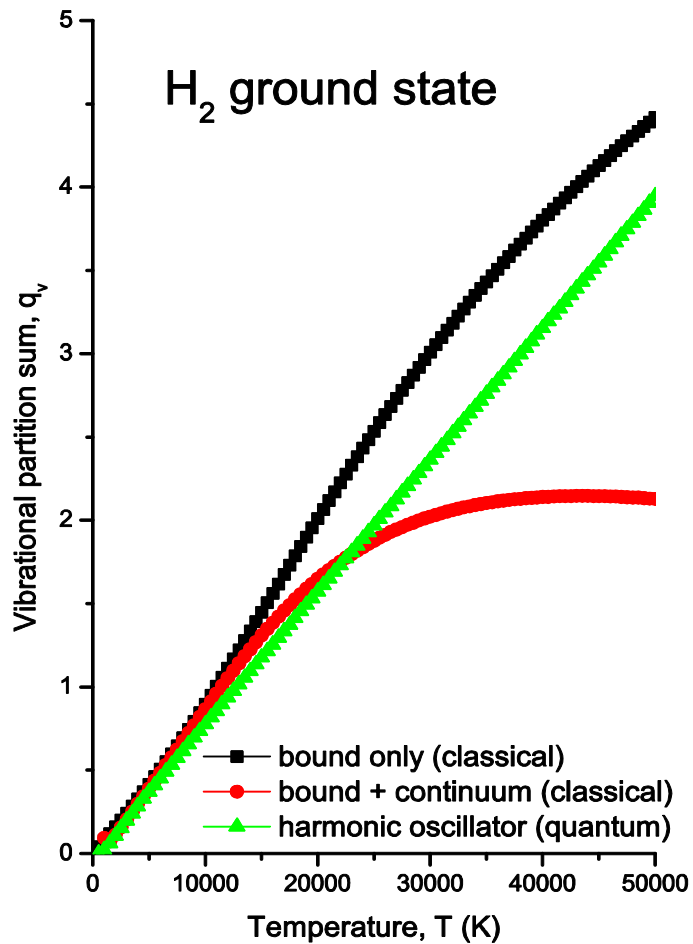
H2



Influence of the quasi-bound and continuum levels

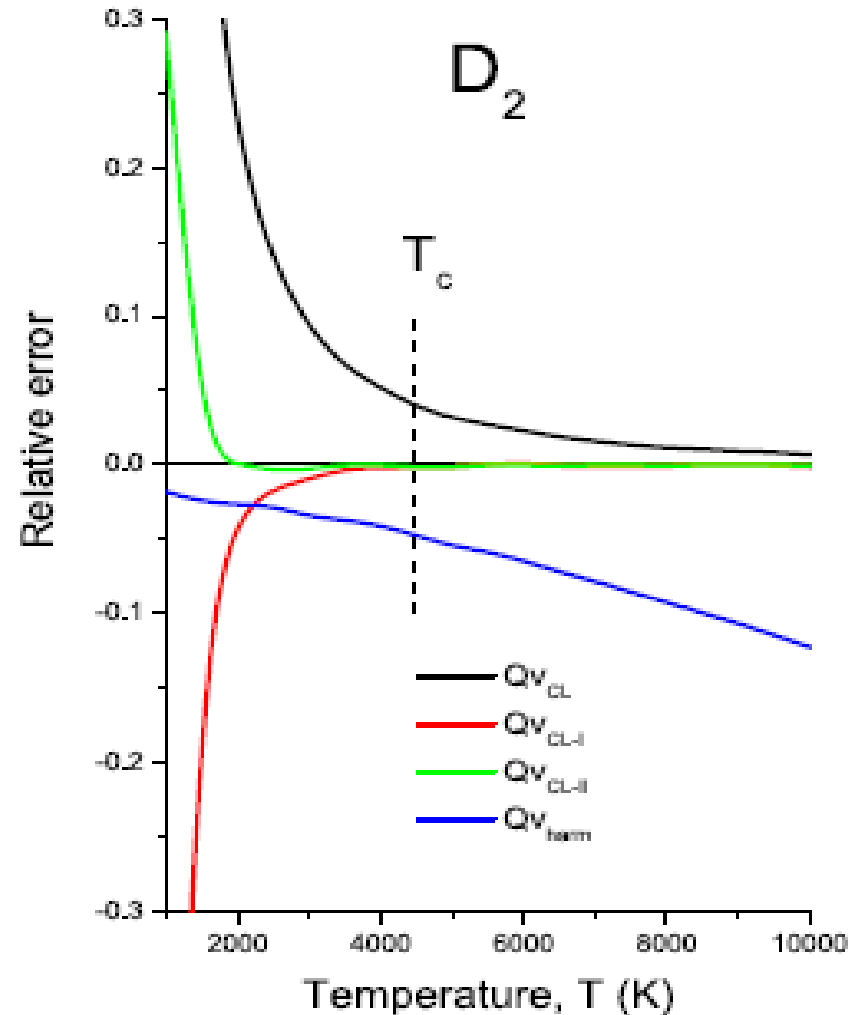
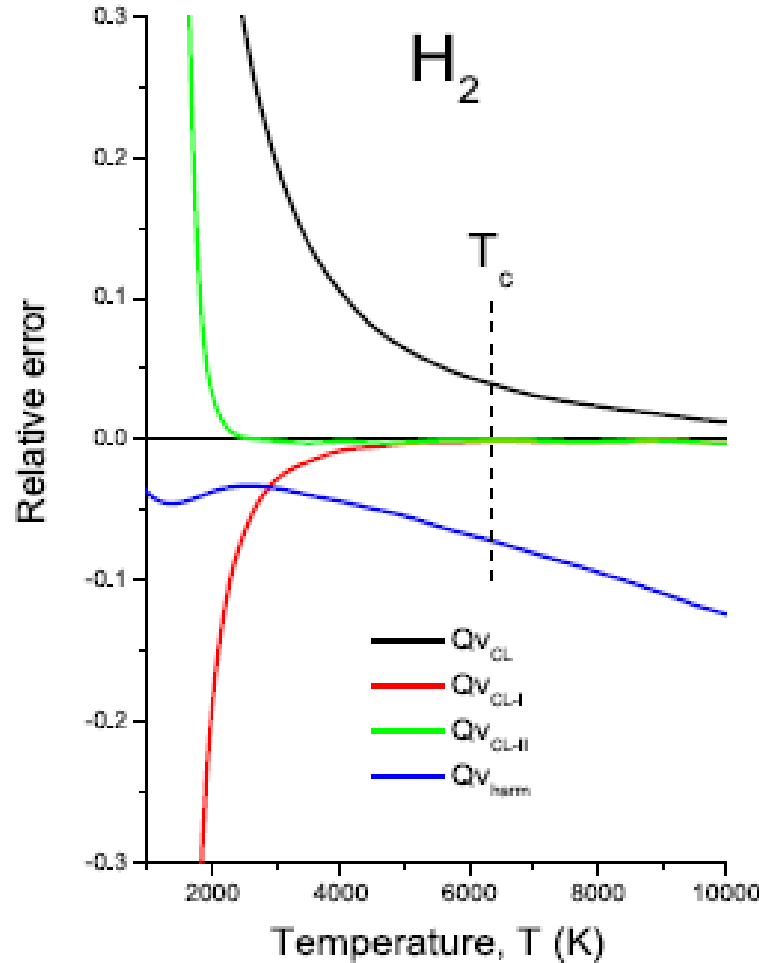


Classical method application to hydrogen molecule



$$T_c = \frac{\omega_e}{k_B}$$

Quasi-classical correction to the classical estimates



Concluding Remarks

- ❑ At **high temperatures** the molecular thermodynamic functions could be evaluated by classical method with a good accuracy (a few percents)
- ❑ At **elevated temperatures** $T \approx \omega_e/k_B$ quasi-classical correction improves the accuracy
- ❑ In the quantum method **all states contribution** should be taken into account

Advantages of the classical method

- ❑ It implicitly takes into account of all three components of spectra: bound, quasi-bound and continuum while the bound state partition could be separated
- ❑ It can be readily generalized for polyatomic molecules as well since the eigen values are not required explicitly. Only potential energy surface (PES) is really needed
- ❑ **Spectroscopic constants are not needed anymore?!**
(it allows one to avoid extrapolation of the spectroscopic constants out of range of their experimental determination)

Thank you for the attention !!!

The work has been supported by

- the Russian Foundation of Basic Research
(grants 10-01-00544-a and 11-03-00307-a)
- the 7 framework program (theme 9, Space)
(grant FP7/2007-2013)