Finite Size Scaling and Quantum Criticality

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Finite Size Scaling and Quantum Criticality

(1) Introduction: Criticality and Finite Size Scaling

(2) Finite Size Scaling in Quantum Mechanics:
How it works

(3) Stability of Matter:
- (a) Atoms
- (b) Molecules
- (c) Quantum Dots

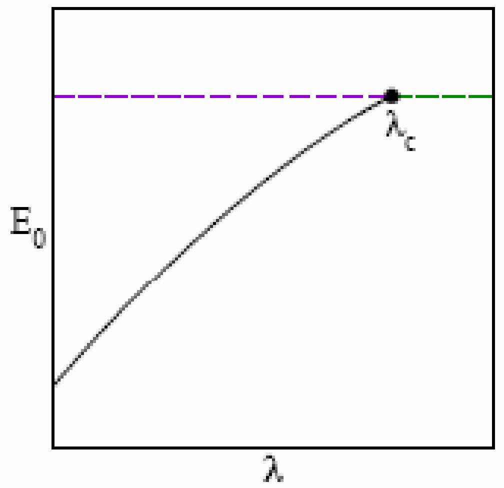
(4) Stabilization in Superintense Laser Fields

(5) Future Work: Open Problems

Quantum Criticality

$$H(\lambda) = H_0 + \lambda V$$

where H_0 and V are λ − independent



we assume that $\exists\ \lambda_c > 0\ H(\lambda)$

$*$ Has at least one bound state for $\lambda < \lambda_c$

$*$ Has no bound states for $\lambda > \lambda_c$

$*\ \lambda = \lambda_c$ depends on $H(\lambda)$

Critical point λ_c: a point for which the ground (bound) state becomes absorbed or degenerate with the continuum

$*$ Critical parameter λ_c

$$E_0(\lambda_c) = \lim_{\lambda \to \lambda_c} E_0(\lambda)$$

$$E_0(\lambda < \lambda_c) \to \text{bound state}$$

$*$ Critical exponent α

$$E_0(\lambda) - E_0(\lambda_c) \sim (\lambda_c - \lambda)^{\alpha} \quad \text{for } \lambda \to \lambda_c$$

Finite Size Scaling

In statistical mechanics, the finite size scaling method provides a systematic way to extrapolate information obtained from a finite system to the thermodynamic limit

Importance

The existence of phase transitions is associated with singularities of the free energy. These singularities occur only in the thermodynamic limit.

Yang and Lee ***Phys. Rev. 87, 404 (1952)***

FSS scaled variable $y = N/\xi(\lambda)$, where ξ is the correlation length of the infinite system.

$$\begin{cases} y \sim 1 & \text{Critical effects are expected to occur} \\ y >> 1 & \text{Bulk-like behavior} \\ y << 1 & \text{Finite-size effects are manifested} \end{cases}$$

If a thermodynamical quantity K develops a singularity as a function of λ in the form

$$K = \lim_{N\to\infty} K_N(\lambda) \sim |\lambda - \lambda_c|^{-\rho}$$

and in particular for the correlation length

$$\xi(\lambda) = \lim_{N\to\infty} \xi_N(\lambda) \sim |\lambda - \lambda_c|^{-\nu}$$

the FSS ansatz assumes that

$$K_N(\lambda) \sim K(\lambda) f_K(y)$$

where $f_K(y)$ is an analytical function. For a finite N, K_N is also analytical, so the behavior of $f_K(y)$ must be

$$f_K(y) \underset{y\to 0}{\sim} y^{\rho/\nu}$$

It follows that at λ_c

$$K_N(\lambda_c) \sim N^{\rho/\nu} \qquad N \to \infty$$

If $\mathrm{K}^{(\mathrm{q})}(\lambda)$ is the qth derivative of $\mathrm{K}(\lambda)$, $\mathrm{K}^{(\mathrm{q})}(\lambda)$ is also singular at λ_c

$$\frac{d^q}{d\lambda^q} K(\lambda) = K^{(q)}(\lambda) \sim \left|\lambda - \lambda_c\right|^{-\rho-q}$$

and therefore

$$K_N^{(q)}(\lambda_c) \sim N^{(\rho+q)/\nu} \quad ; N \to \infty$$

Since $K^N(\lambda)$ is an analytical function in λ, it has a Taylor expansion around λ_c and $K_N(\lambda)$ can be expressed as

$$K_N(\lambda) \sim N^{\rho/\nu}\phi_K(N^{1/\nu}|\lambda-\lambda_c|), \qquad N \to \infty$$

where ϕ_K is a scaling function which is regular around λ_c.

We can apply FSS to the correlation length ξ.

$$\xi_N(\lambda) \sim N\phi_\xi(N^{1/\nu}|\lambda - \lambda_c|), \qquad N \to \infty$$

Nightingale developed the phenomenological renormalization (PR) equation for finite systems of sizes N and N′ is given by

$$\frac{\xi_N(\lambda)}{N} = \frac{\xi_{N'}(\lambda')}{N'}$$

In the present approach, the finite size corresponds not to the spatial dimension, as in statistics, but to the number of elements in a complete basis set used to expand the exact eigenfunction of a given Hamiltonian.

Quantum Mechanics

$$\psi = \sum_{n=0}^{\infty} a_n \phi_n \cong \sum_{n=0}^{M} a_n \phi_n$$

(Variational Calculations)

Classical $(N \to \infty)$	$\Leftrightarrow$	Quantum $(M \to \infty)$

Phys. Rev. Letters 79, 3142 (1997)

Finite Size Scaling: Quantum Mechanics

$$H = H_0 + V_\lambda$$

$$\psi_\lambda^{(N)} = \sum_n^{M(N)} a_n^{(N)}(\lambda)\phi_n$$

The FSS ansatz

$$\langle O \rangle_\lambda^{(N)} \sim \langle O \rangle_\lambda F_O\left(N|\lambda - \lambda_C|^\nu\right)$$

$$\Delta_O(\lambda; N, N') = \frac{\ln\left(\langle O \rangle_\lambda^{(N)} / \langle O \rangle_\lambda^{(N')}\right)}{\ln(N'/N)}$$

The curves intersect at the critical point

$$\Delta_O(\lambda_C; N, N') = \Delta_O(\lambda_C; N'', N)$$

Short Range Potentials
Yukawa Potential

Hamiltonian

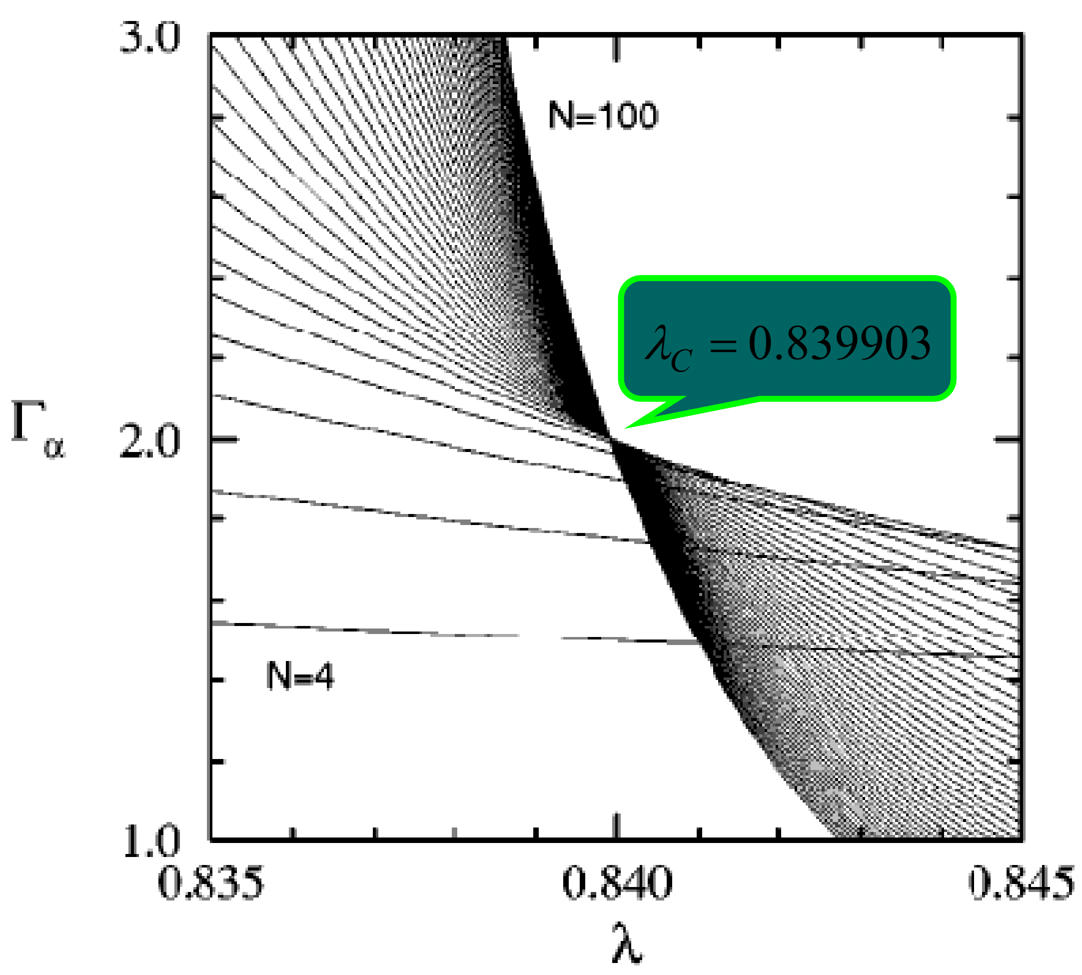
$$H(\lambda) = -\frac{1}{2}\nabla^2 - \lambda\frac{e^{-r}}{r}$$

Basis Set

$$\phi_n(r,\Omega) = \frac{1}{\sqrt{(n-l+1)(n-l+2)}} e^{-r/2} L_{n-l}^{(2)}(r) Y_{l,m}(\Omega)$$

Where $L_{n-l}^{(2)}(r)$ is the Laguerre polynomial of degree n and order 2 and $Y_{l,m}(\Omega)$ are the spherical harmonic functions of the solid angle

Yukawa



$$\Gamma_\alpha = \frac{\Delta_H}{\Delta_H - \Delta_{\frac{\partial V}{\partial \lambda}}}$$

$$\lambda_c^{exact} = 0.839908$$

Phys. Rev. A 57, R1481 (1998)

Finite Size Scaling with Gaussian Basis Sets

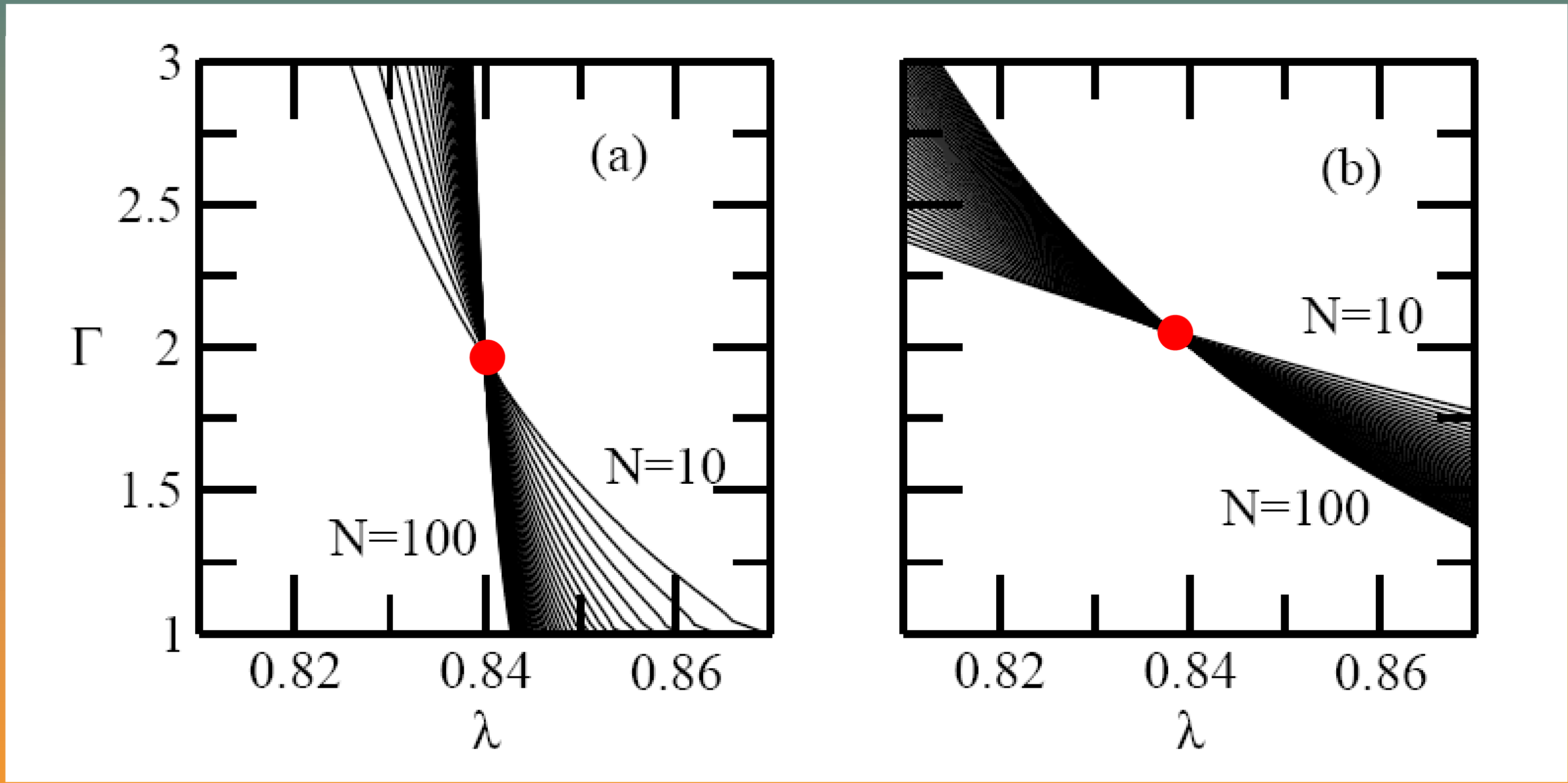
The main idea is to use Gaussian basis sets to do FSS calculations for large atomic and molecular systems.

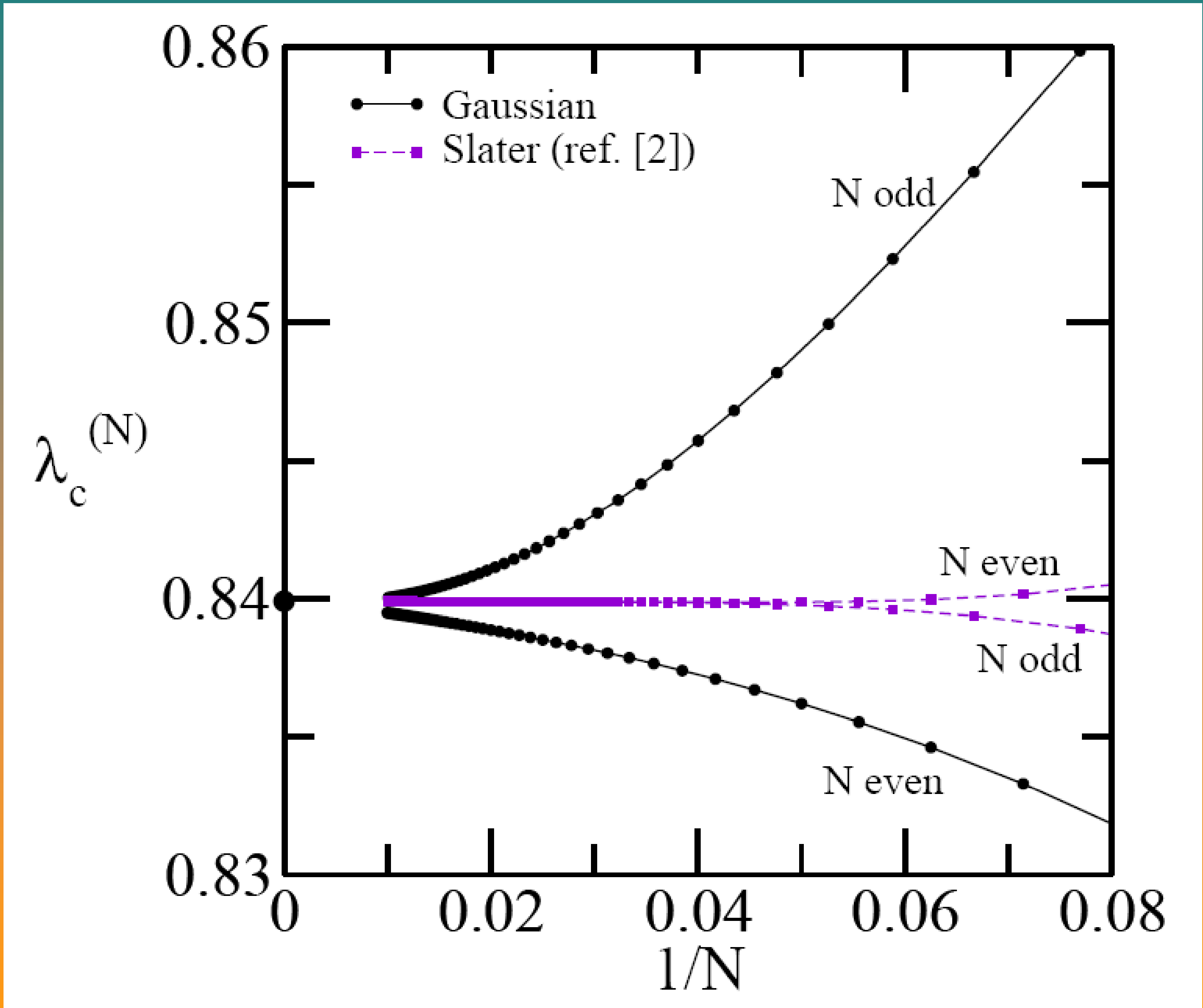
The basis-set is an over-complete set of Gaussian functions:

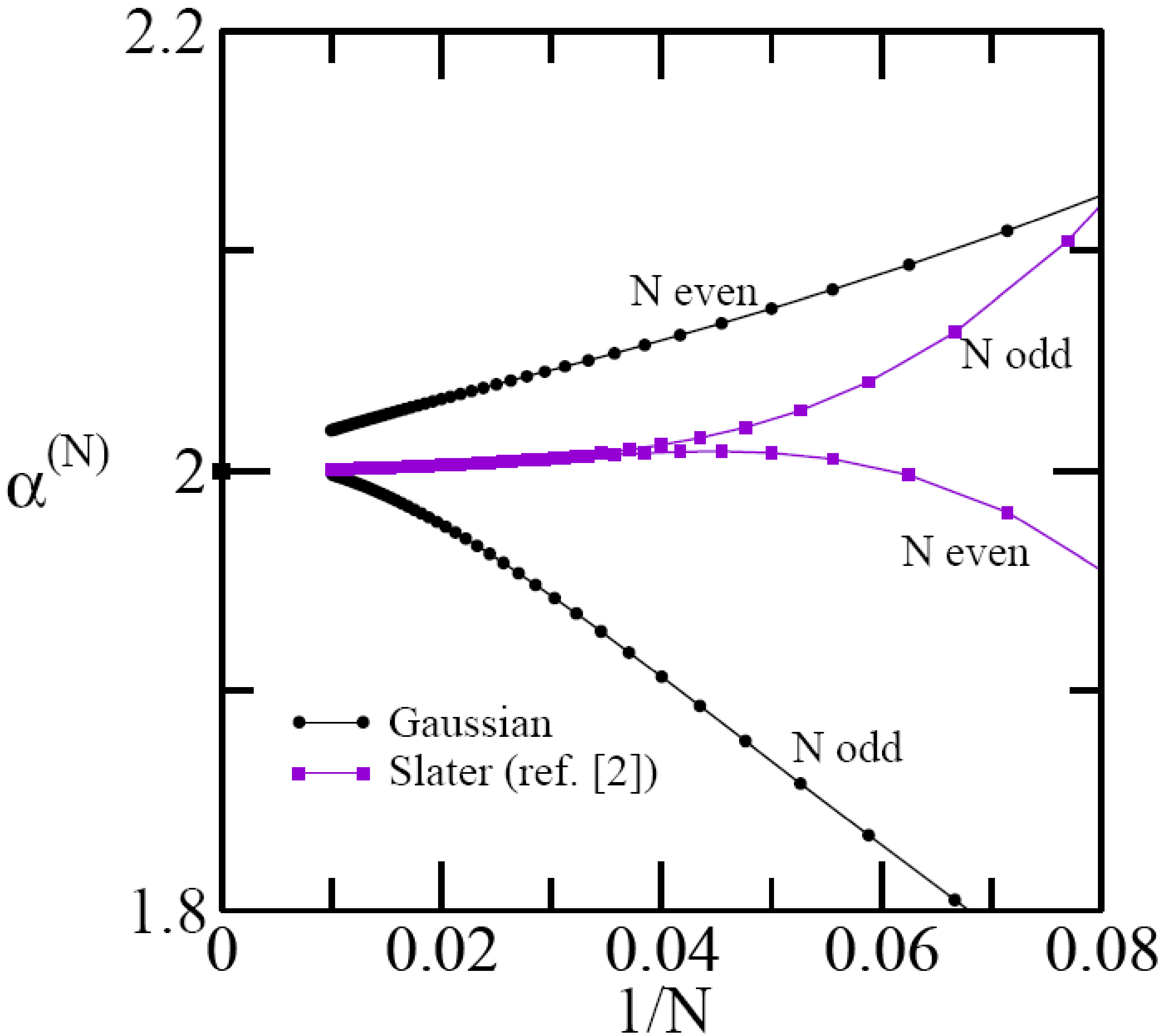
$$\phi_{i,j,k}(\beta;\vec{x}) = C_{ijk}\exp(-\beta r^2)x^i y^j z^k$$

Where C_{ijk} are the normalization constants and β is a free parameter.

Gaussians **Slater**




Gaussian
Slater (ref. [2])
N odd
N even
N even
N odd
0.86
0.85
0.84
0.83
0
0.02
0.04
0.06
0.08
1/N
$\lambda_c^{(N)}$


2.2
2
1.8
0
0.02
0.04
0.06
0.08
1/N
$\alpha^{(N)}$
N even
N odd
N even
N odd
Gaussian
Slater (ref. [2])

Finite Size Scaling
Data Collapse

$$\langle O \rangle_\infty \underset{\lambda \to \lambda_C^+}{\sim} (\lambda - \lambda_C)^\mu$$

$$\langle O \rangle_N \sim \langle O \rangle_\infty F_O\left(N|\lambda - \lambda_C|^\nu\right)$$

$$F(x) \underset{x \to 0}{\sim} x^{-\mu/\nu}$$

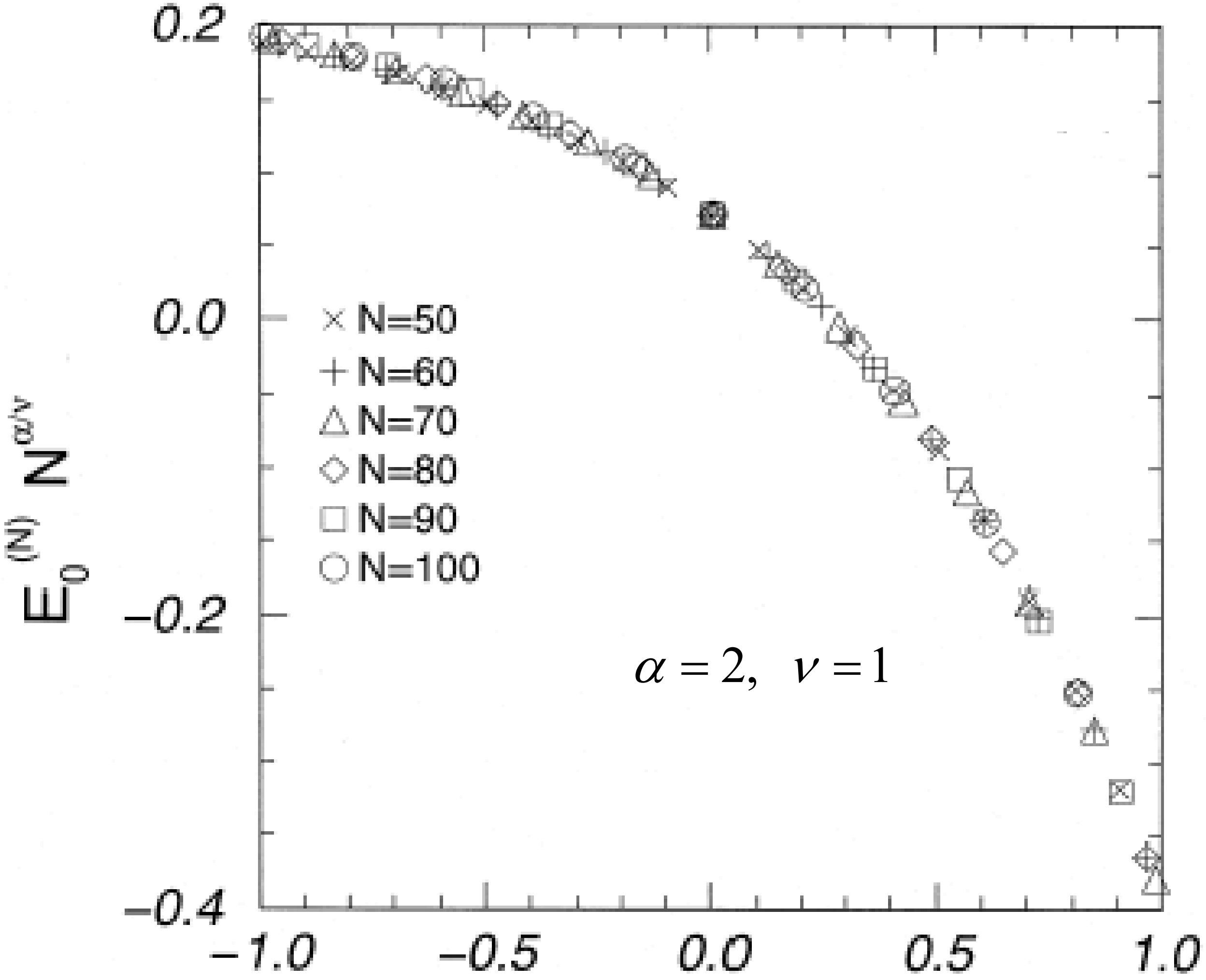
$$\langle O \rangle_N \underset{N \to \infty}{\sim} N^{-\mu/\nu}$$

$$\langle O \rangle_N \sim N^{-\mu/\nu} G\left(N^{1/\nu}(\lambda - \lambda_C)\right)$$

$$E_0 N^{\alpha/\nu} \sim G\left(N^{1/\nu}(\lambda - \lambda_C)\right)$$

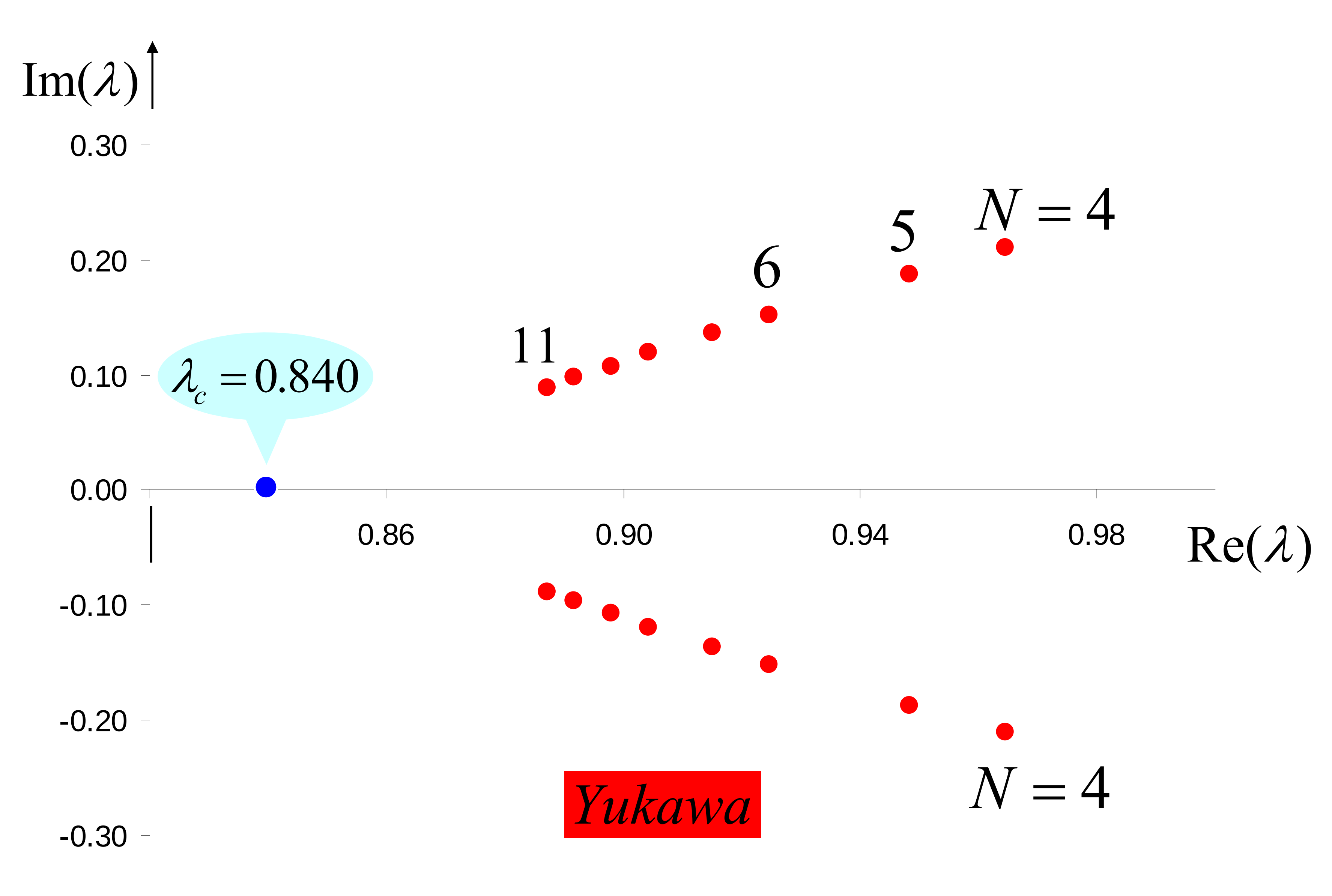
Data Collapse

$$E_0 N^{\alpha/\nu} \sim G\left(\left(\lambda-\lambda_C\right)N^{1/\nu}\right)$$



$$\left(\lambda-\lambda_C\right)N^{1/\nu}$$

Chem. Phys. Letters 319, 273 (2000)



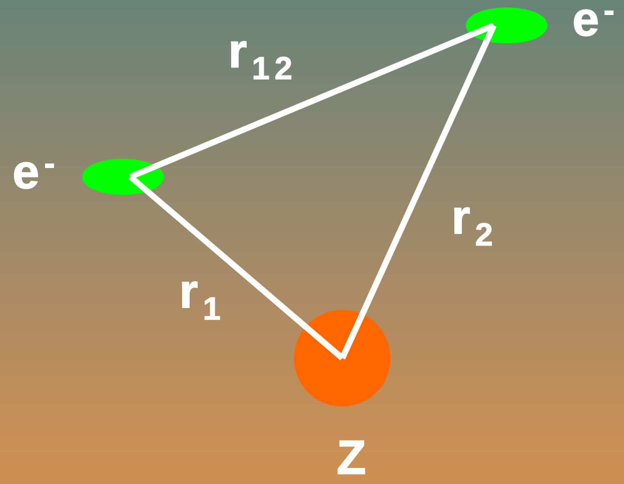
Chem. Phys. Letters 423, 45 (2006)

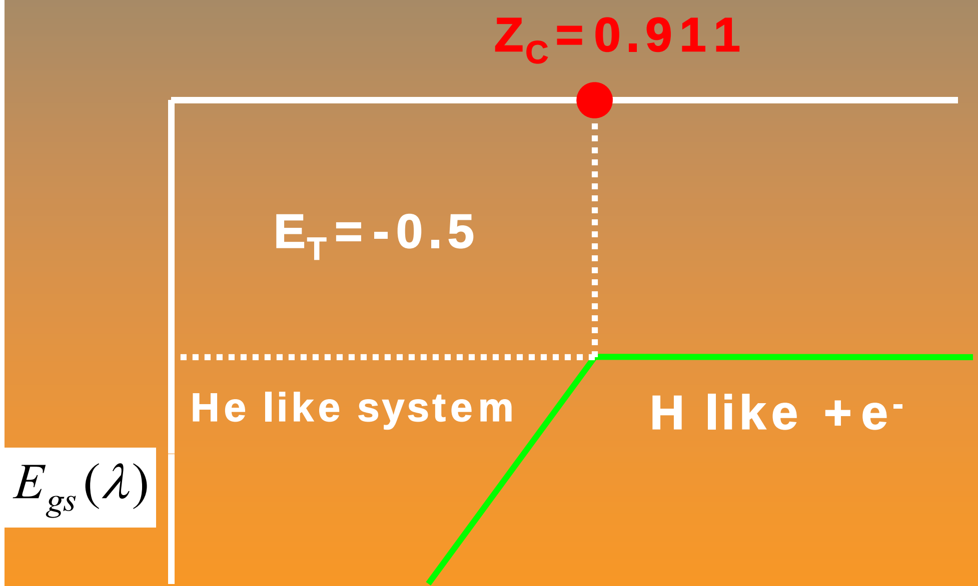
Two Electrons Atoms

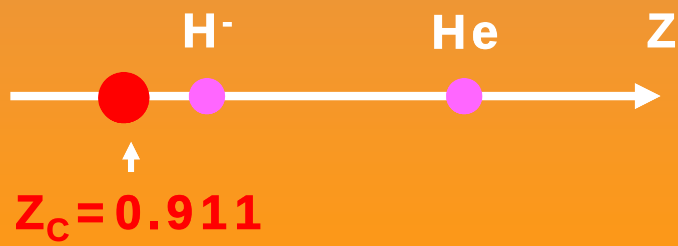
$$H(\lambda) = -\frac{1}{2}\nabla_1^{\ 2} - \frac{1}{2}\nabla_2^{\ 2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}}$$

$$\lambda = \frac{1}{Z}$$

$$r_{12} = |r_1 - r_2|$$







Finite Size Scaling procedure

❖ **Hamiltonian:**

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}}; \quad \lambda = \frac{1}{Z}$$

❖ **Basis Set:**

$$\Psi = \sum_{i,j,k} C_{i,j,k} \frac{1}{\sqrt{2}} \left(r_1^{\,i} r_2^{\,j} e^{-\alpha r_1 - \beta r_2} + r_1^{\,j} r_2^{\,i} e^{-\beta r_1 - \alpha r_2} \right) r_{12}^{\,k}$$

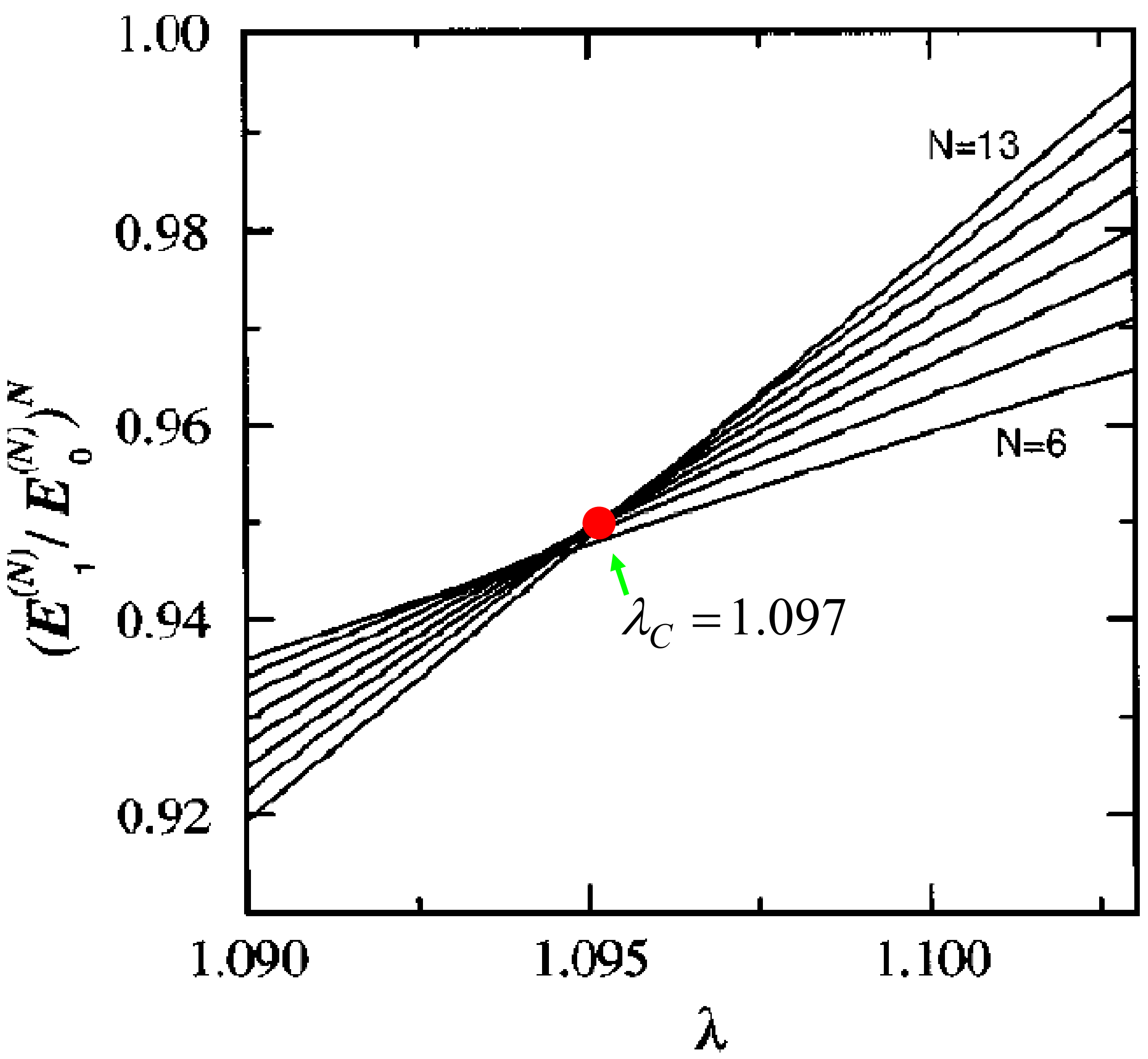
$$i + j + k \leq N$$

❖ **Hamiltonian Matrix:**

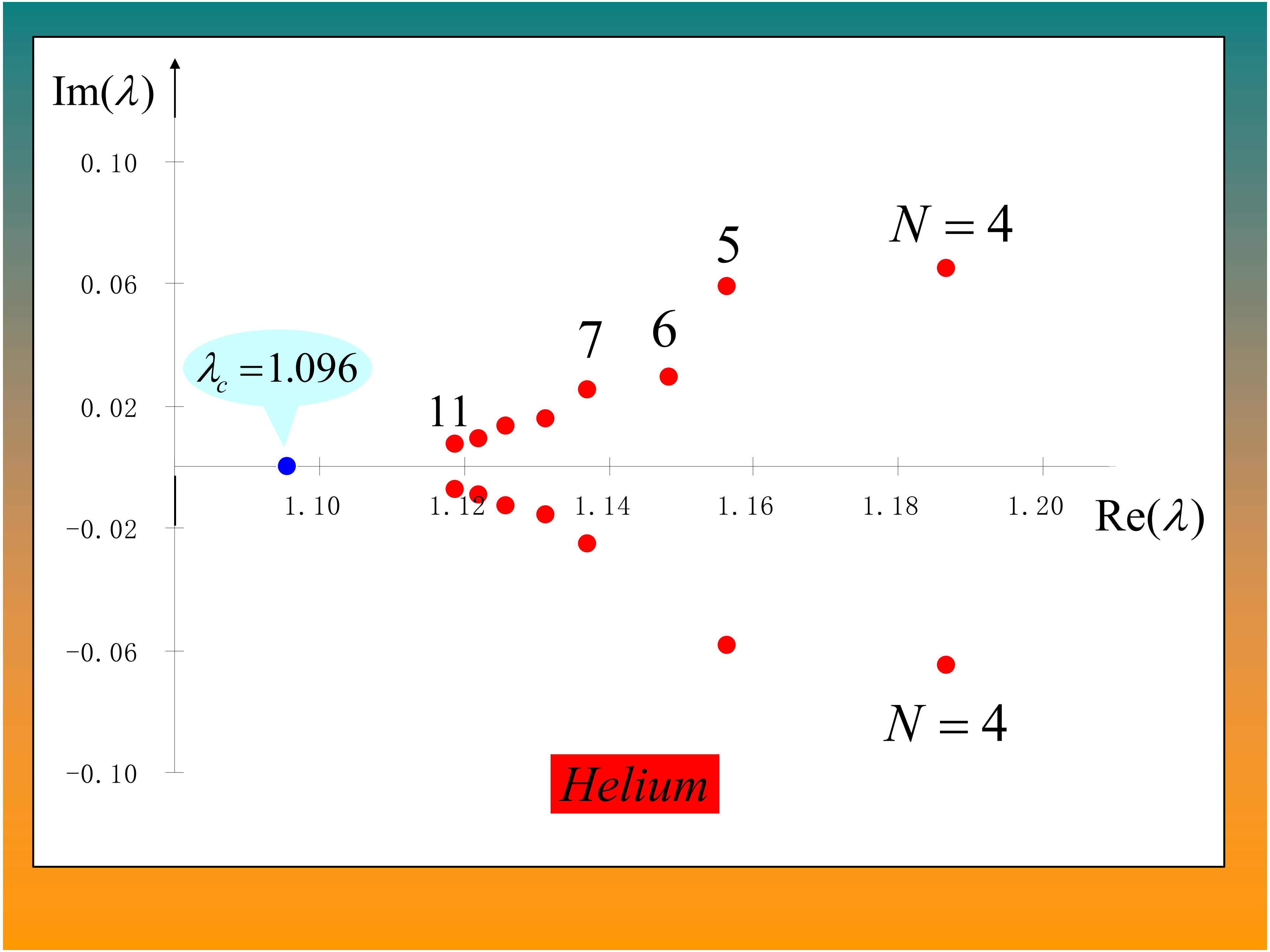
Leading Eigenvalues, E_0, E_1

❖ **Renormalization Equation:**

$$\left(\frac{E_1(N)}{E_0(N)} \right)^{N} = \left(\frac{E_1(N+1)}{E_0(N+1)} \right)^{N+1}$$

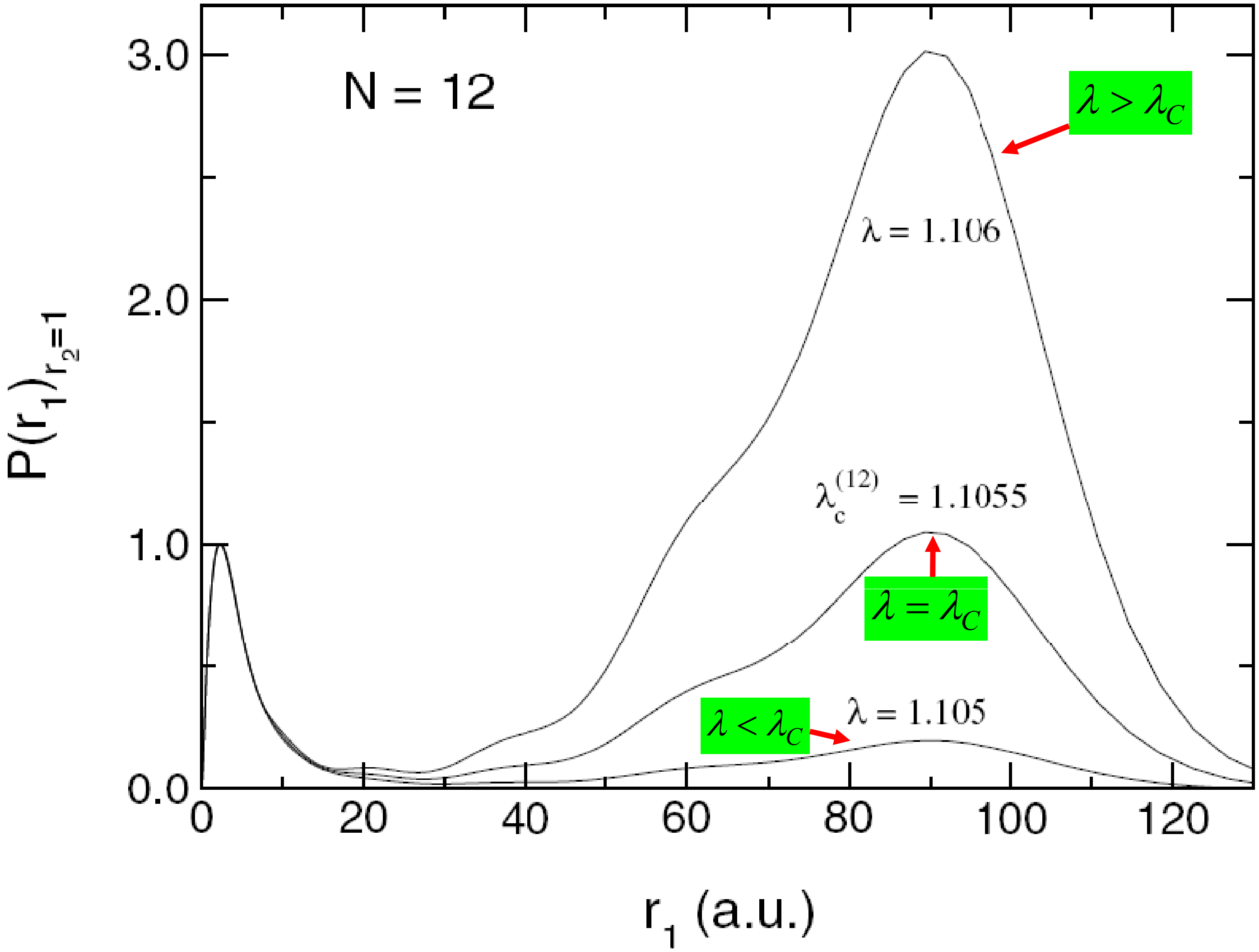


Phys. Rev. Letters 80, 5293 (1998)



Im(λ)
0.10
0.06
0.02
−0.02
−0.06
−0.10
$\lambda_c = 1.096$
11
7
6
5
$N = 4$
1.10
1.12
1.14
1.16
1.18
1.20
Re(λ)
$N = 4$
Helium

Conditional Probability



Critical of Shannon Information Entropy

Shannon proposed that the information entropy for a system with a continuous probability distribution P(x) in one dimension could be characterized as

$$S = -\int P(x) \ln P(x) dx \,; \quad \int P(x) dx = 1$$

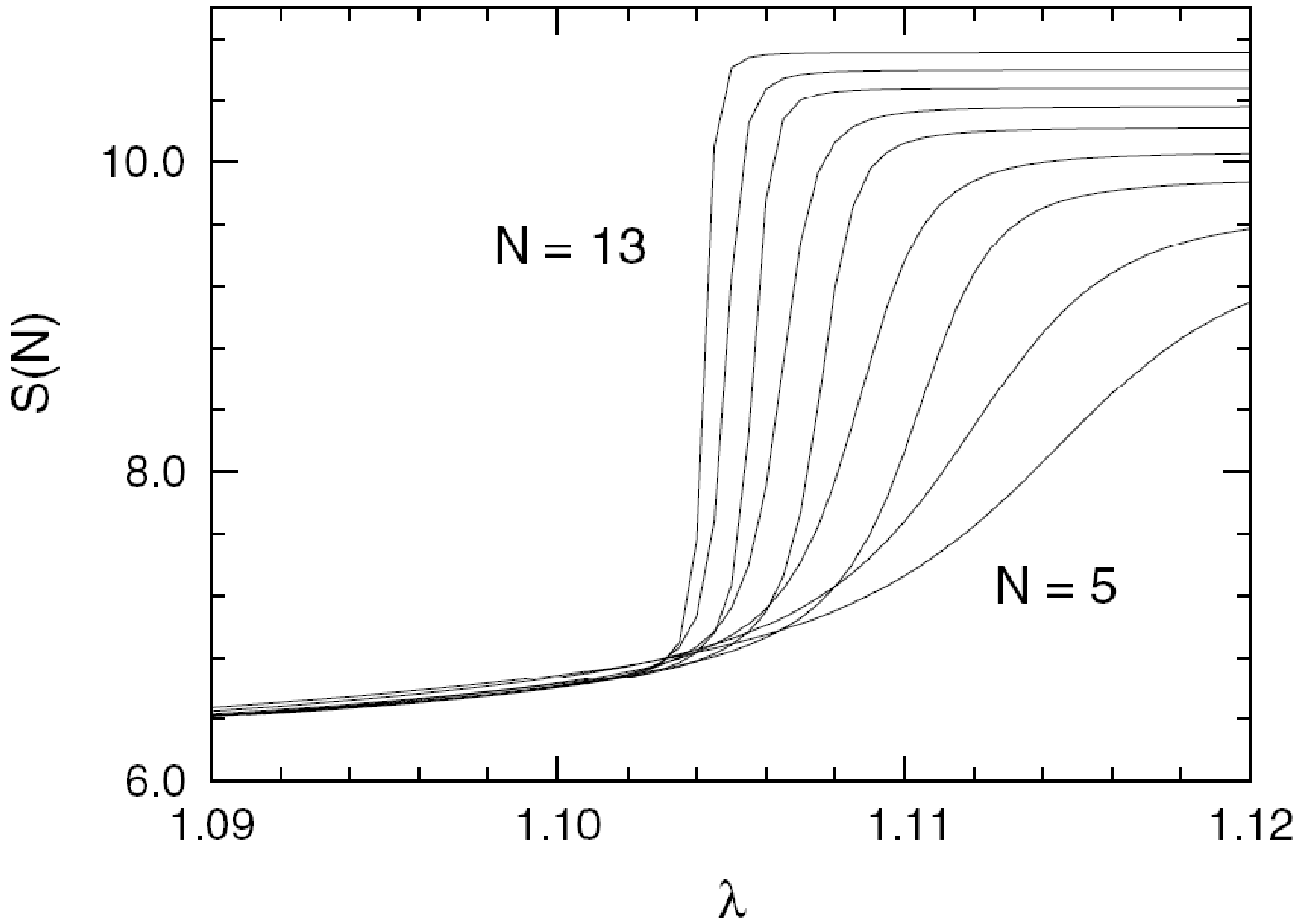
Electronic Structure

Shannon information entropy for electronic charge distribution ρ(r) is given by

$$S = -\int_0^\infty \rho(r) \ln \rho(r) 4\pi r^2 dr$$

S measures the delocalization or the lack of structure in the respective distribution.

$$S = -\int \rho \ln \rho dV$$



Chem. Phys. 309, 127 (2005)

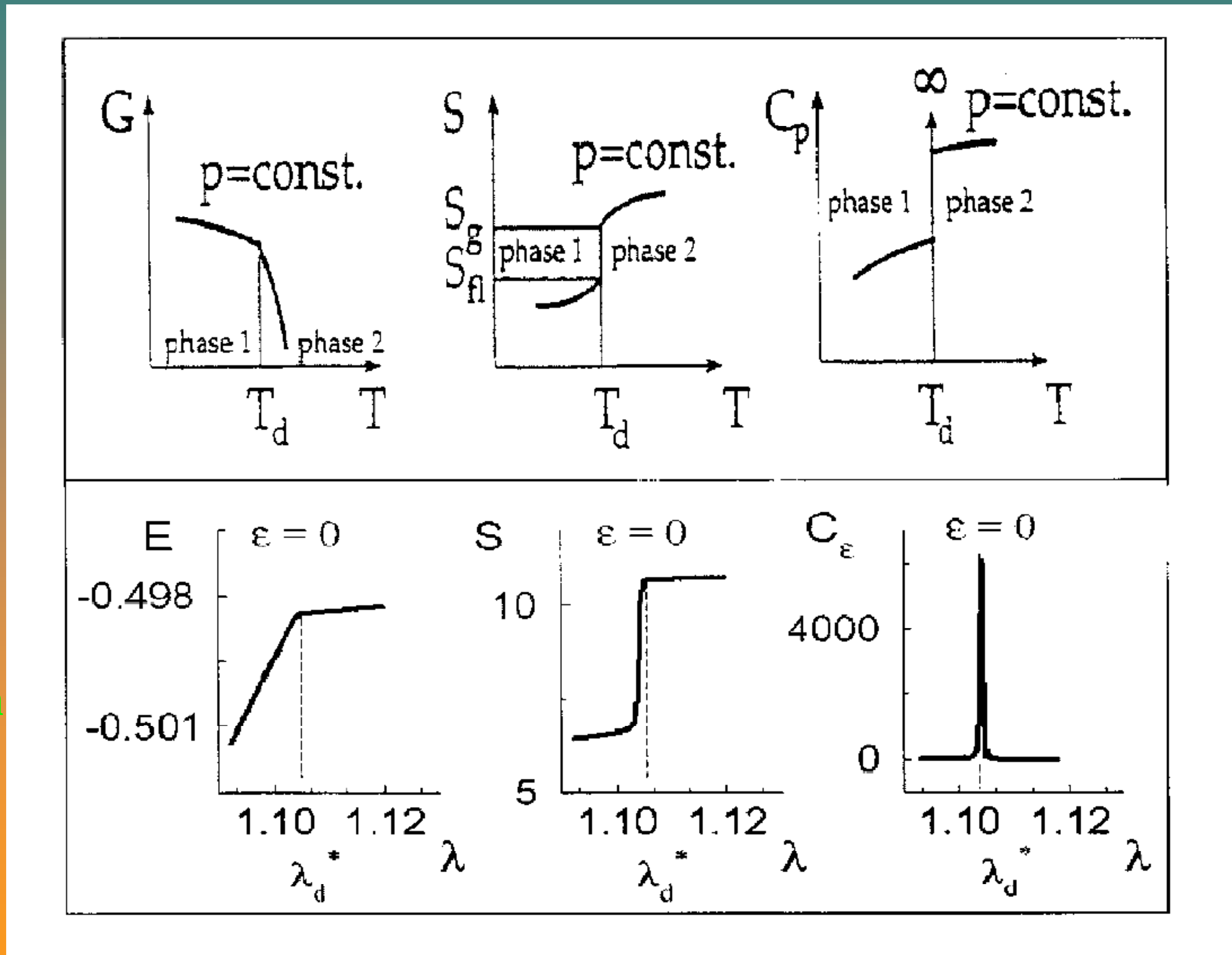
D = 3

Fluids

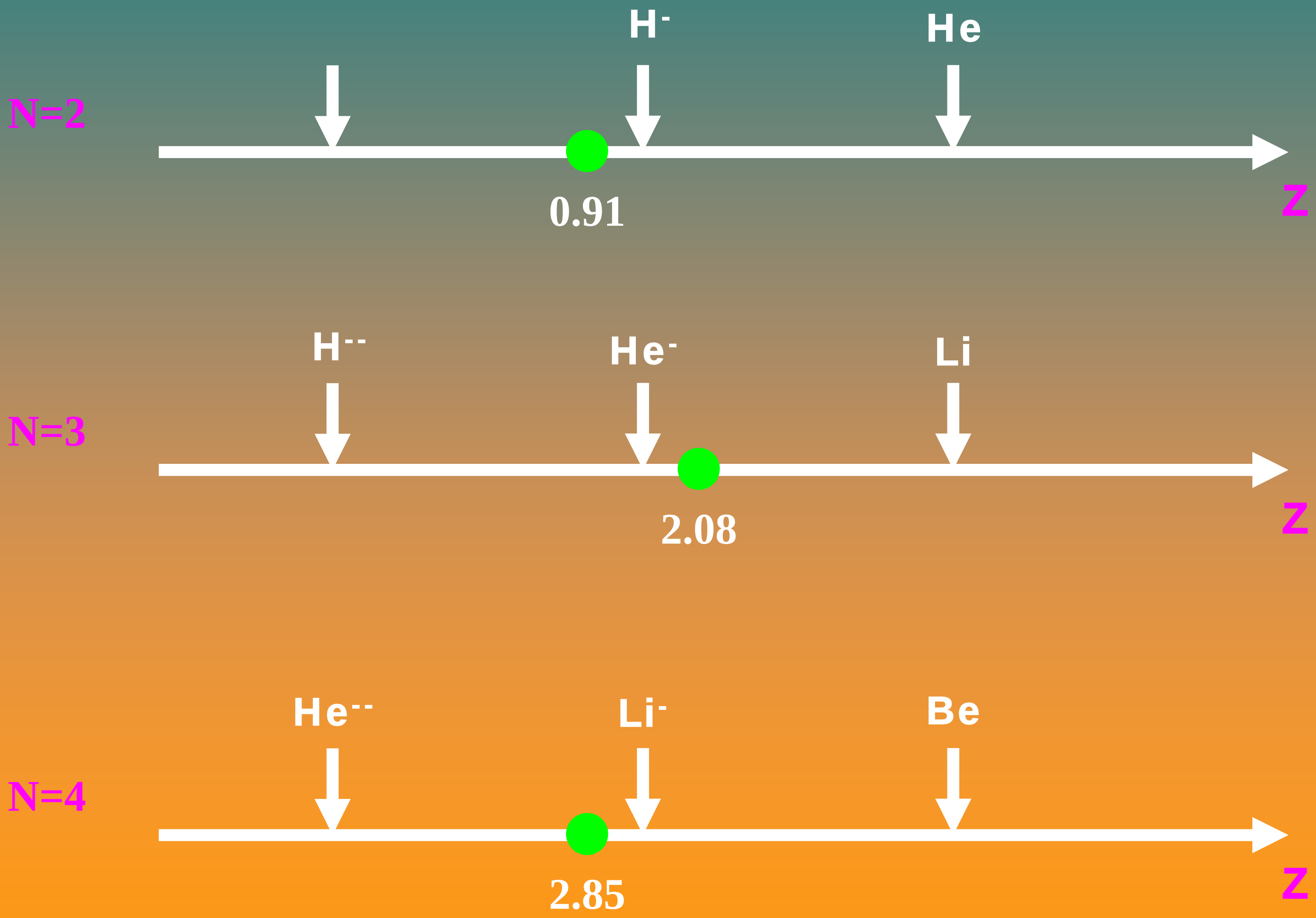
Liquid → Gas

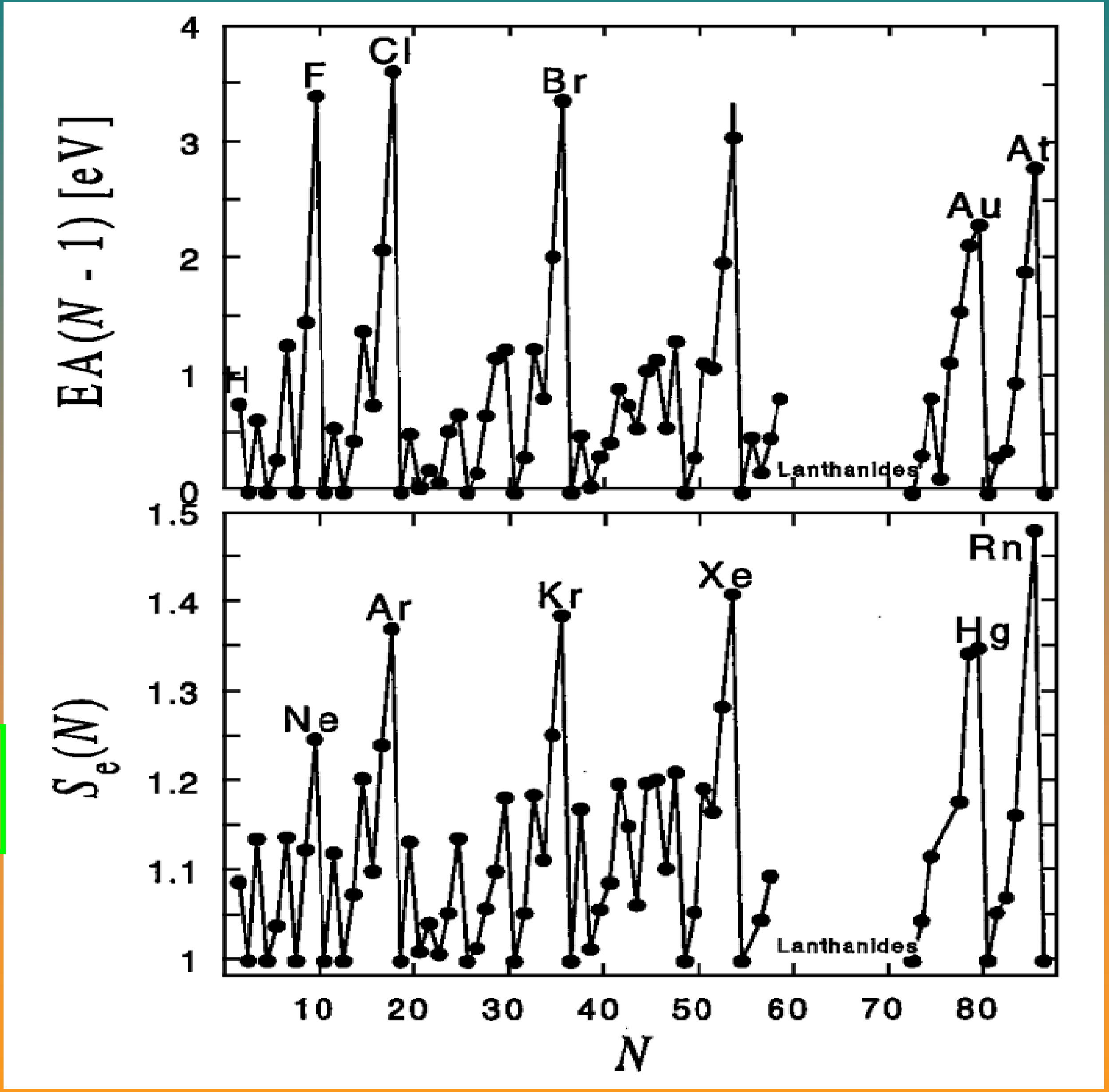
Electronic Structure

Bound → Continuum



Critical Charges and Stable Atoms and Ions





Surcharge
$S_e = N - Z_C$

Int. J. Quantum Chem. 75, 533 (1999)

- **Do doubly charged negative atomic ions exist in the gas phase?**

NO

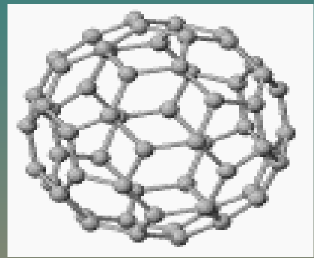
- **What is the smallest object that can bind two extra electrons?**

This is a challenge for experiment and theory!

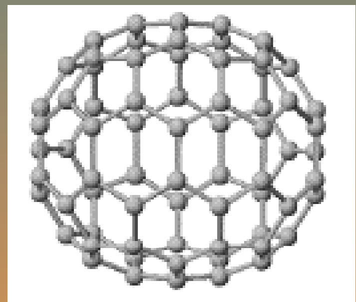
The two electrons must be separated by at least 5.6 Å

Stability of Dianions of Fullerenes

EA1 = + 2.65 eV
EA2 = - 0.3 eV



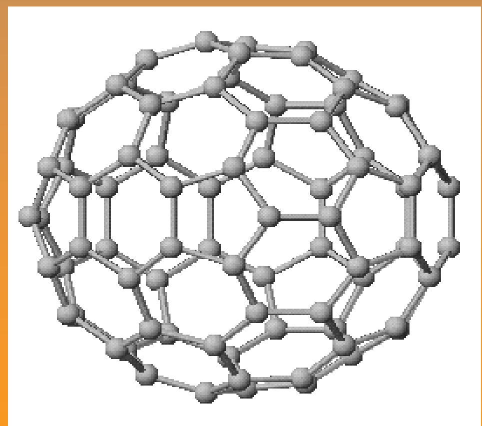
C_{60}^{-}



R_C = 5.6 A

C_{79}^{--}

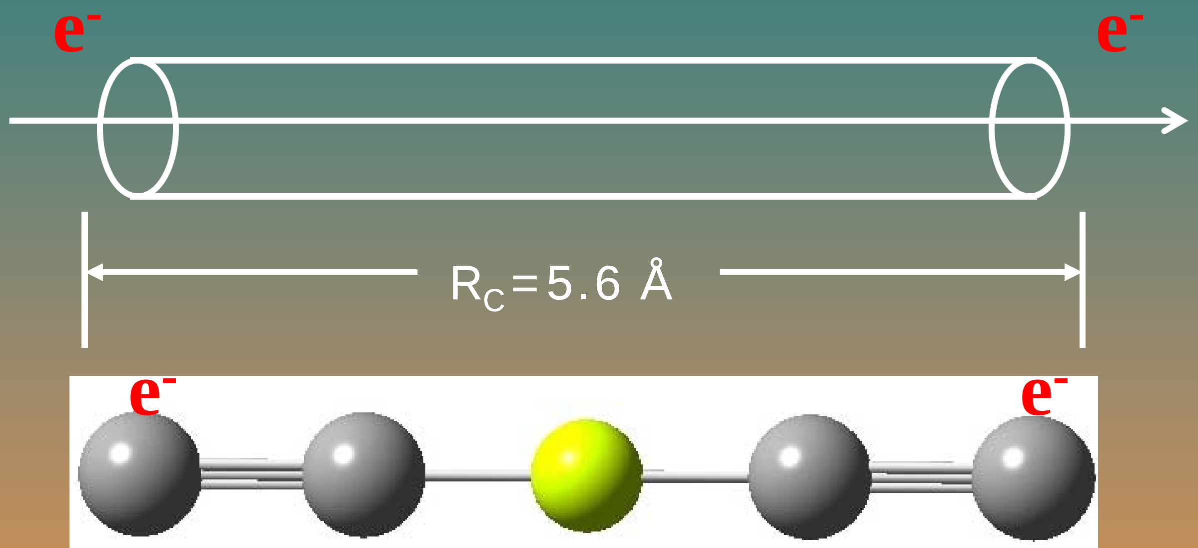
EA1 = + 3.14 eV
EA2 = + 0.44 eV



C_{84}^{--}

Advances in Chemical Physics, Volume 125, 1 (2003).

Stability of Linear Dianions



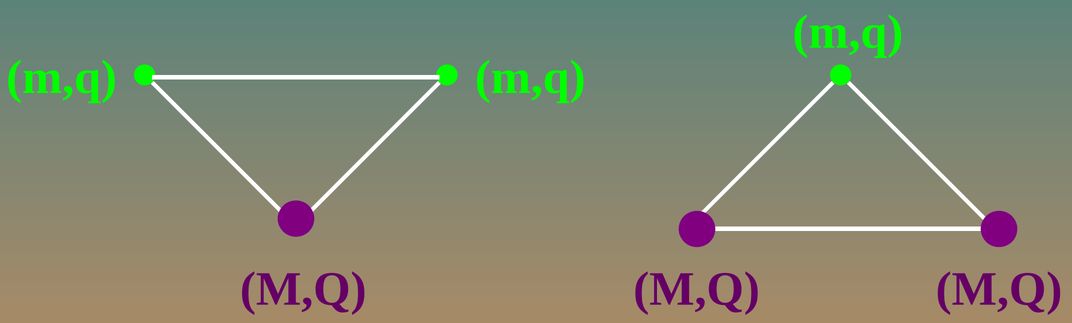
$$^{-}C \equiv C - Be - C \equiv C^{-}$$

$^{1}\Sigma_g^{+}$

BeC_4^{--}

$$BeC_4^{--} \longrightarrow BeC_2^{-} + C_2^{-}$$

Phase Transitions and Stability of Three Body Coulomb Systems



$$\mathrm{He} \leftrightarrow \mathrm{He}^{+} + \mathrm{e}^{-}$$

$$\mathrm{H}_2^{\ +} \leftrightarrow \mathrm{H} + \mathrm{p}$$

$$|Q|/Q = -|q|/q$$

$$r \to fr$$

$$H \to uH/f^2$$

$$f = u|Qq|$$

$$u = \frac{mM}{m+M}$$

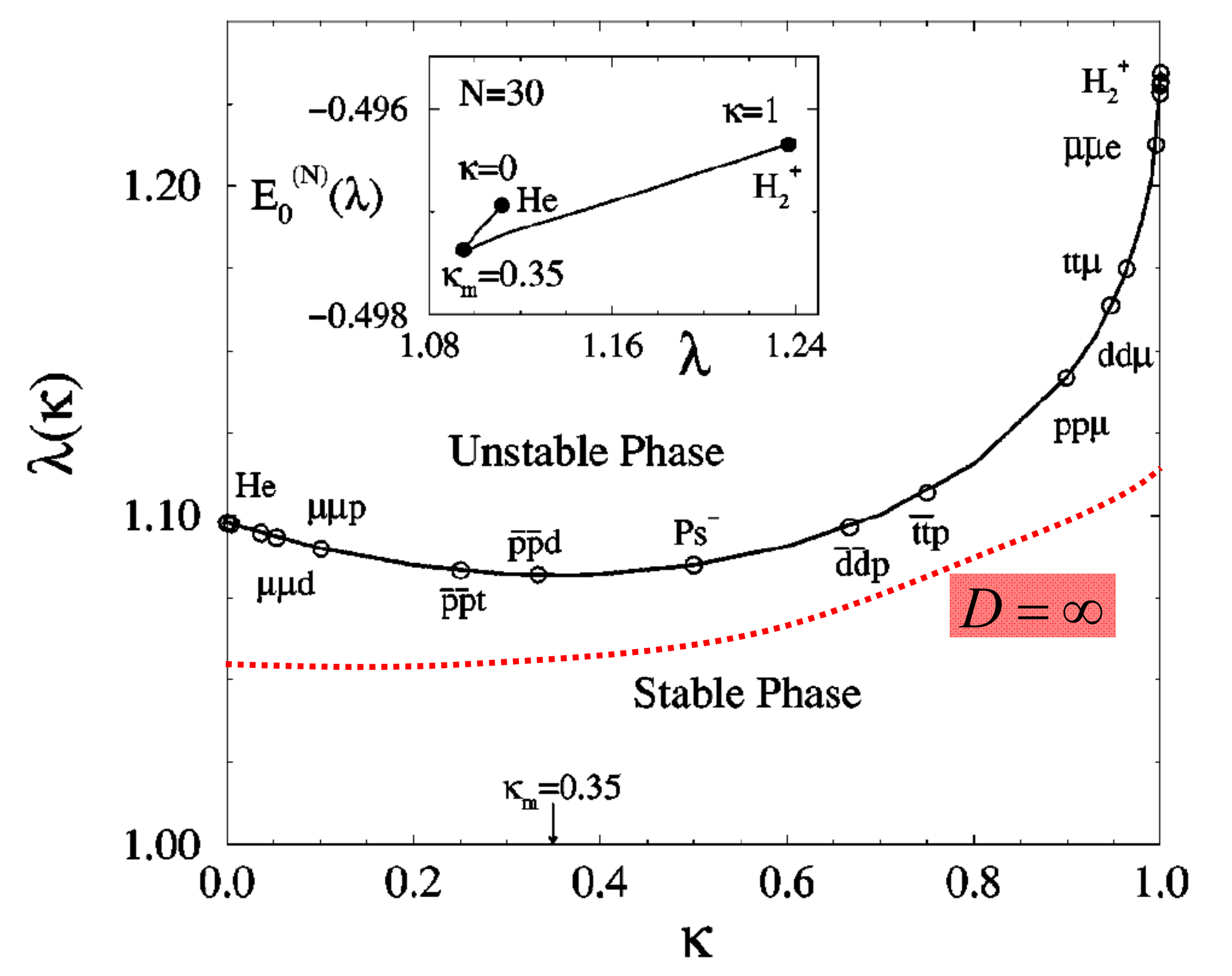
$$H = -\frac{1}{2\mu}\nabla_1^2 - \frac{1}{2\mu}\nabla_2^2 - \frac{1}{m}\nabla_1\cdot\nabla_2 + \frac{qQ}{r_1} + \frac{qQ}{r_2} + \frac{Q^2}{r_{12}}$$

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{1}{r_1} - \frac{1}{r_2} - \kappa\nabla_1\cdot\nabla_2 + \lambda\frac{1}{r_{12}}$$

$$0 \le \lambda = |Q/q| \le \infty$$

$$0 \le \kappa = (1 + m/M)^{-1} \le 1$$

Three Body Coulomb Systems (ABA)



Particles	Mass
e: electron	1
p: proton	1836.15
u: muon	206.76
d: deuteron	3670.5
t: tritium	5476.92

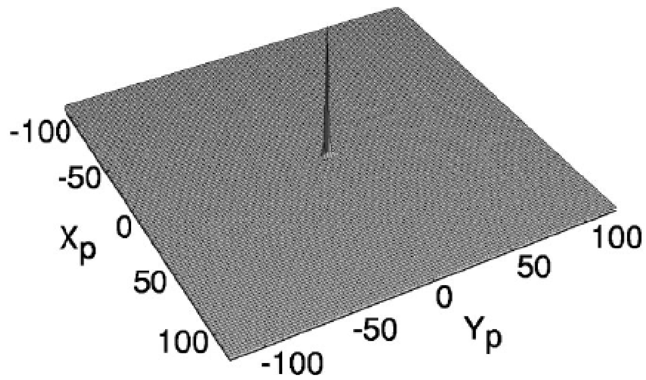
$(e^- \mu^+ e^-)$ Stable $(\mu^- p^+ \mu^-)$ Stable

S. Kais, Phys. Rev. A 62, 06050 (2000)

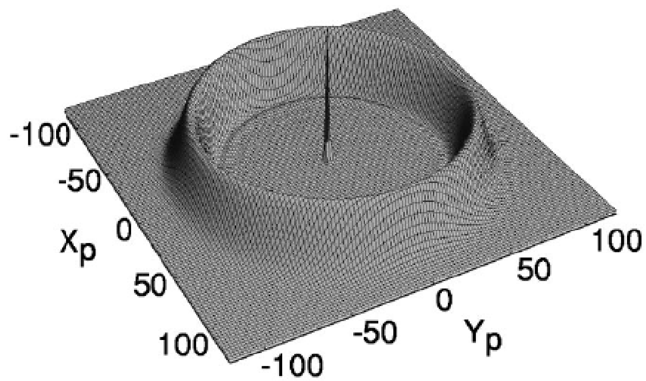
Phase Transitions and Stability of Three Body Coulomb Systems

Charge density probability

H_2^+



(a) $\lambda^{(N=20)} < \lambda_c^{(N=20)}$



(b) $\lambda^{(N=20)} > \lambda_c^{(N=20)}$

$\lambda = 1.24 < \lambda_C^{N=20} = 1.2402$

Bound States

$\lambda = 1.241 > \lambda_C^{N=20} = 1.2402$

Coulomb Explosion

FSS for Critical Conditions for Stable Quadrupole Bound Anions

Hamiltonian: Consists of a charge q at the origin and two charges –q/2 at z = +1 & -1

$$\mathcal{H}(q) = -\frac{1}{2}\nabla^2 - \frac{q}{r} + \frac{q}{2}\left\{\frac{1}{|\vec{r}-\hat{z}|} + \frac{1}{|\vec{r}+\hat{z}|}\right\}$$

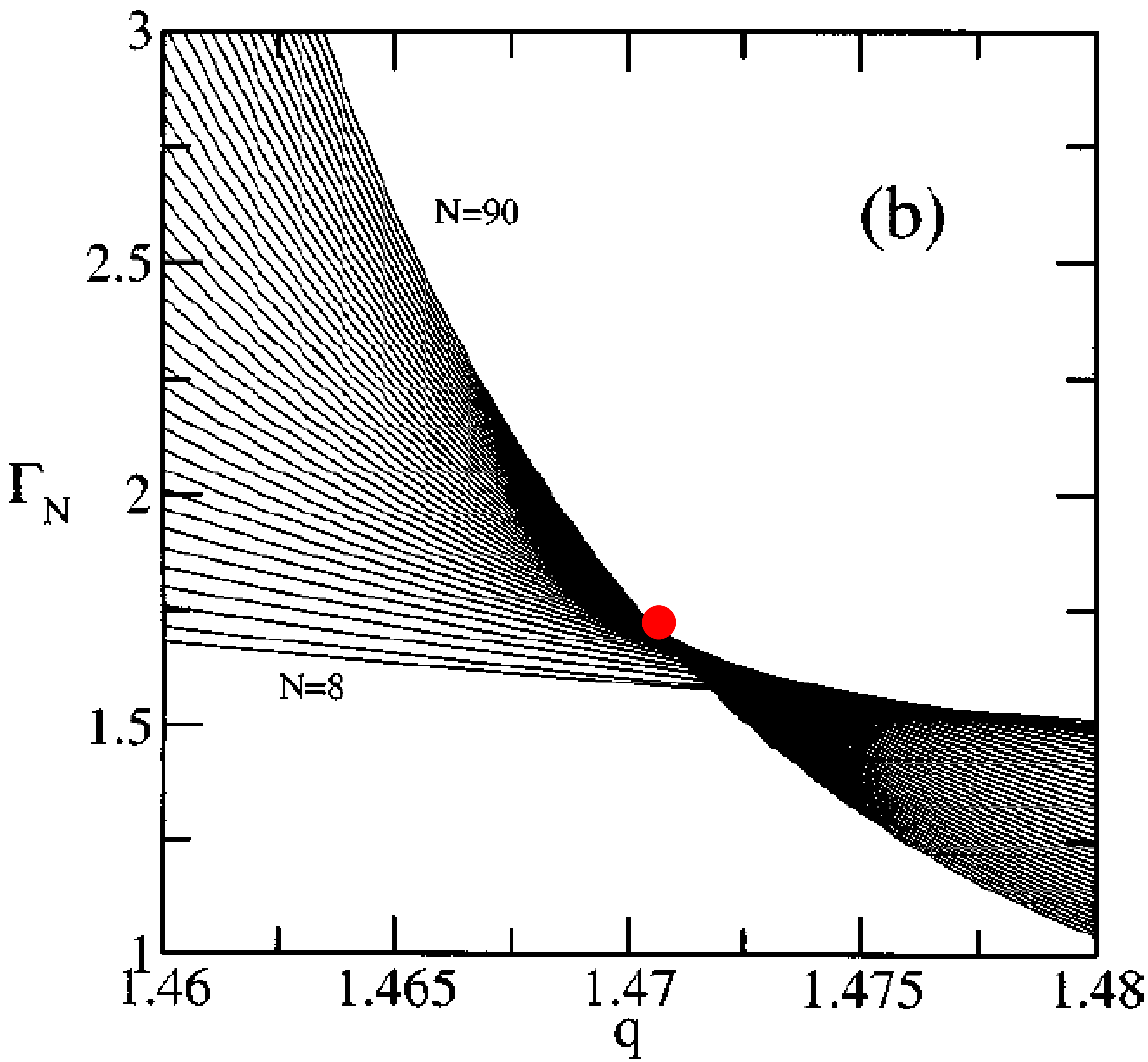
Slater Basis Set:

$$\Phi_{n,l}(\vec{r}) = \left[\frac{4\pi\beta^{2n+3}}{(4l+1)(2n+2)!}\right]^{1/2} e^{-\beta r/2} r^n P_{2l}(\theta)$$

$$n = 0,1,\ldots, \qquad l = 0,1,\ldots,[n/2],$$

Where β is the variational parameter used to optimize the numerical results and $P_{2l}(\theta)$ is the Legendre polynomial of order l.

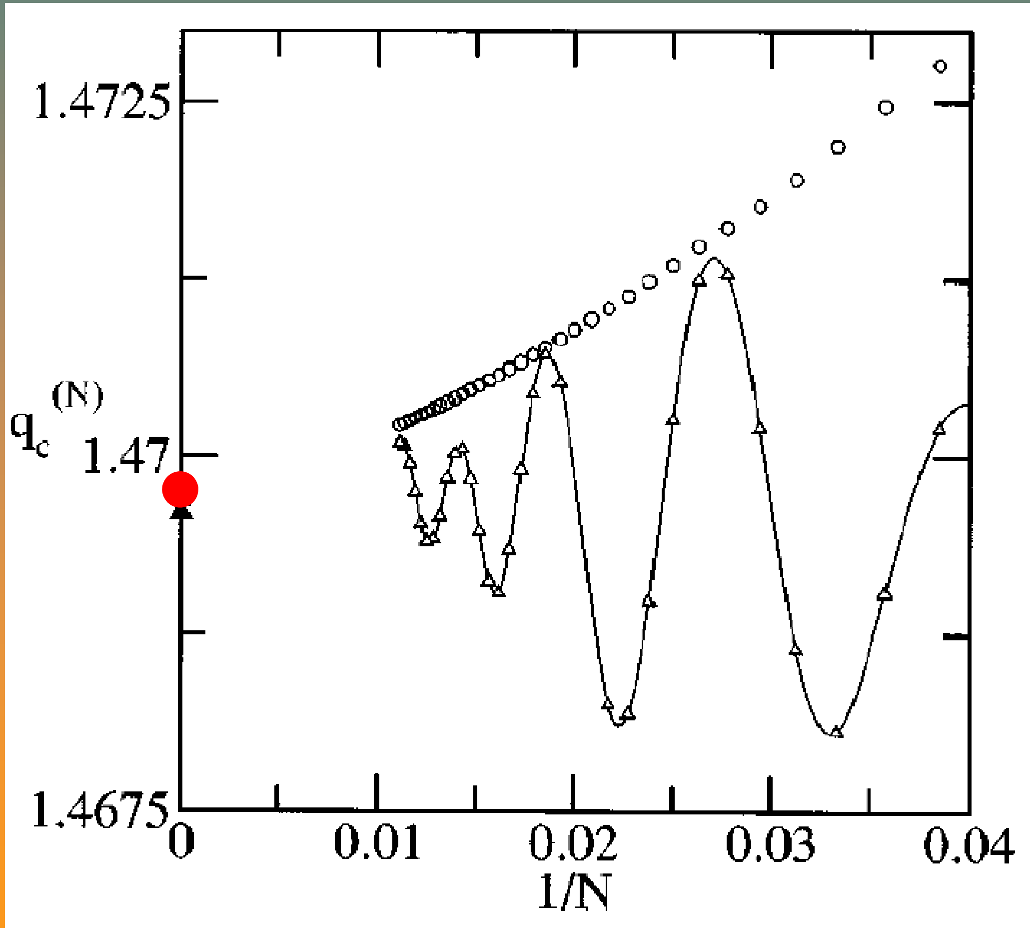
$$q \longrightarrow q = QR$$



Journal of Chemical Physics, 120, 8412 (2004)

$q_c = 1.46$ a.u $\left(-\frac{q}{2}, +q, -\frac{q}{2}\right)$

$q_c = 3.9$ a.u $\left(+\frac{q}{2}, -q, +\frac{q}{2}\right)$



KCl_2^- $Q_{zz} = 10$ a.u

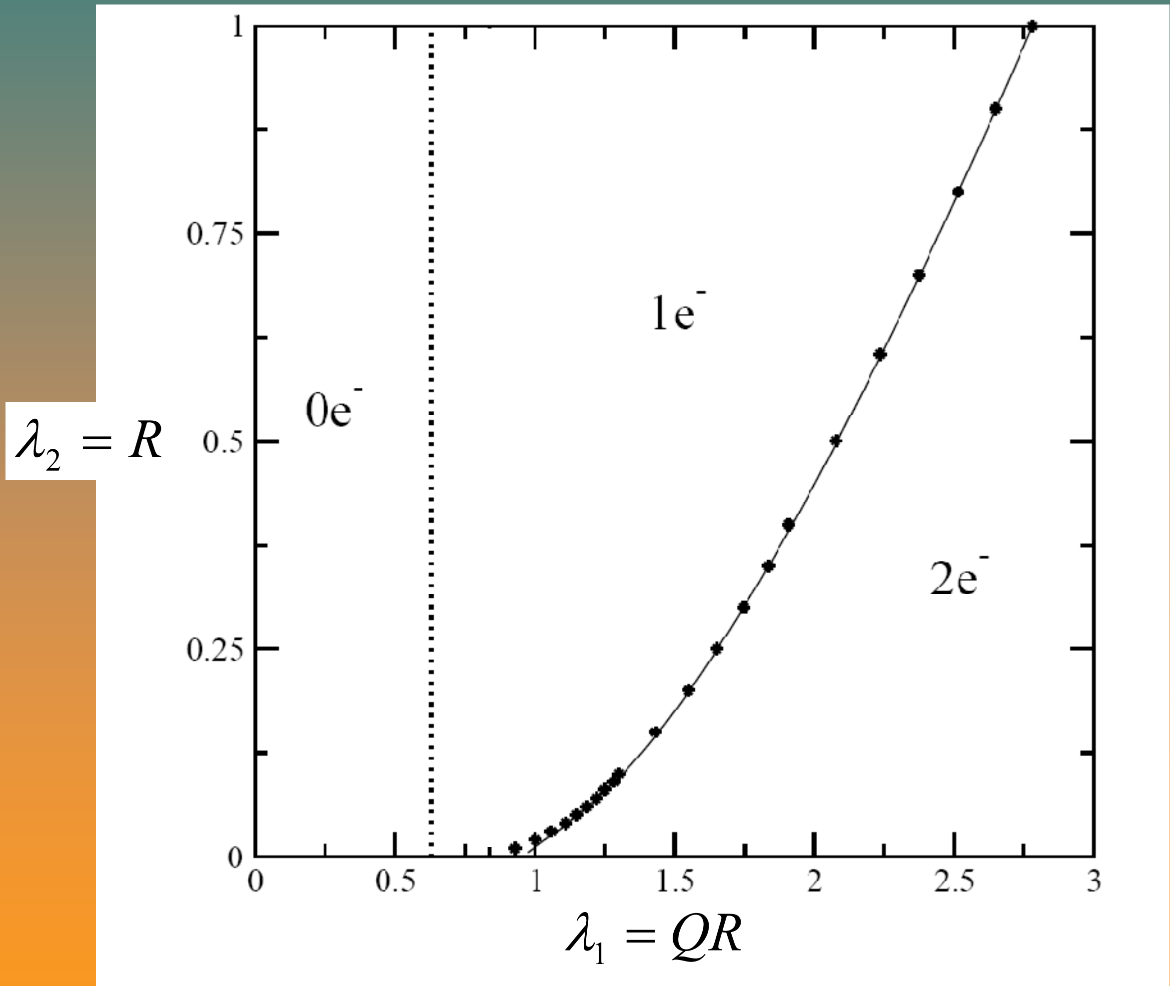
K_2Cl^- $Q_{yy} = 27$ a.u

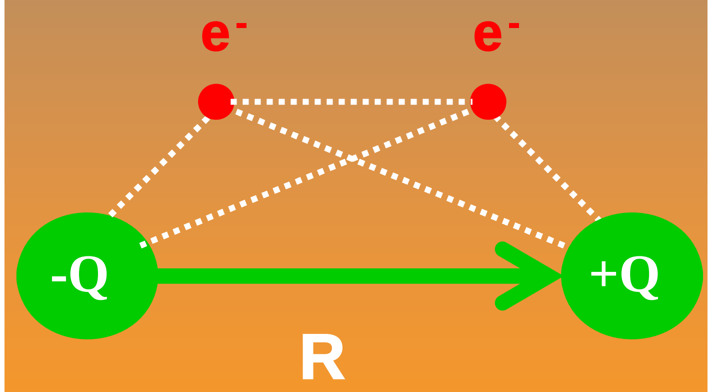
$(BeO)_2^-$ (13,13,0.5)

CS_2^- $Q_{zz} = 4$ a.u

Journal of Chemical Physics, 120, 8412 (2004)

Stability diagram for two electron dipole



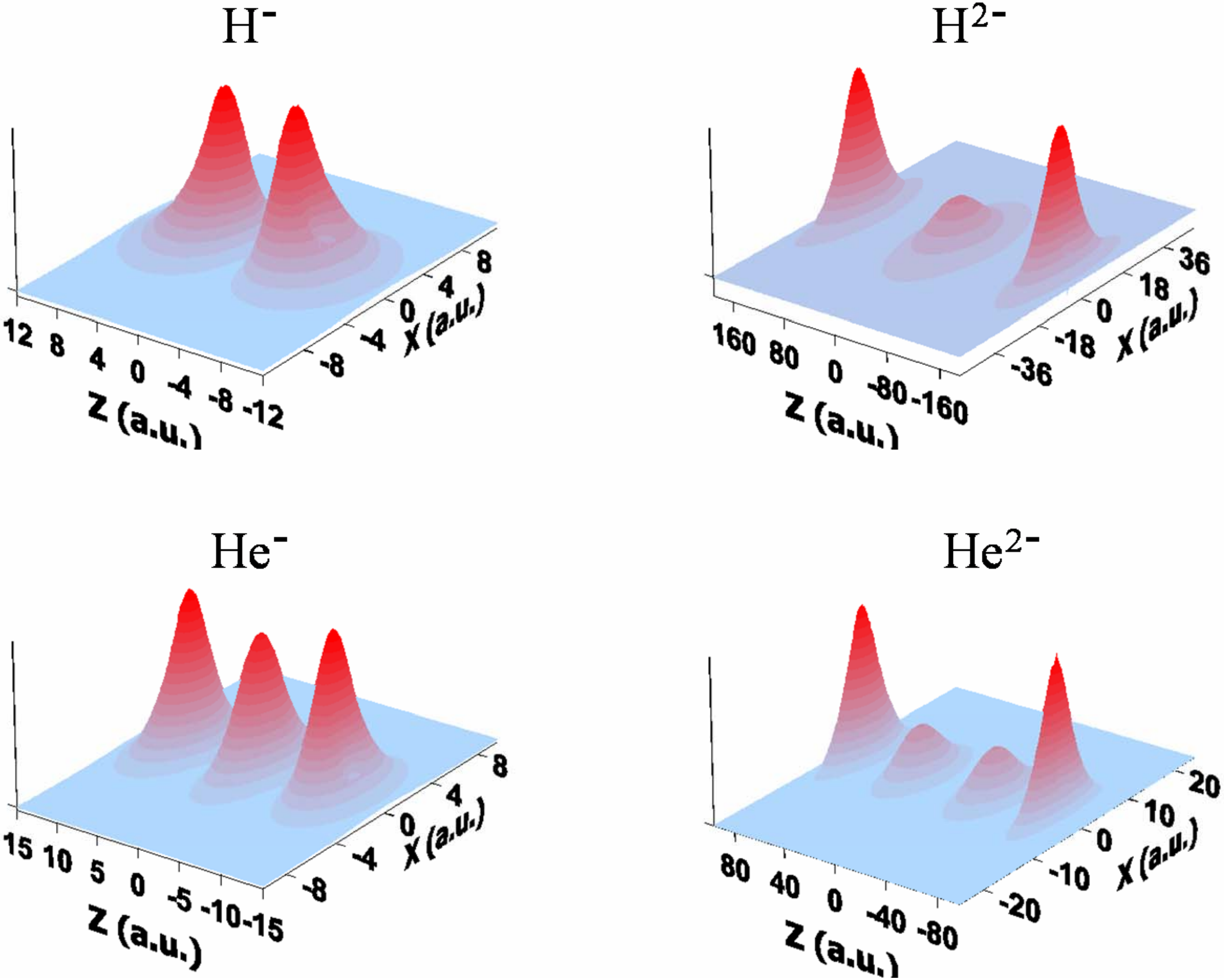


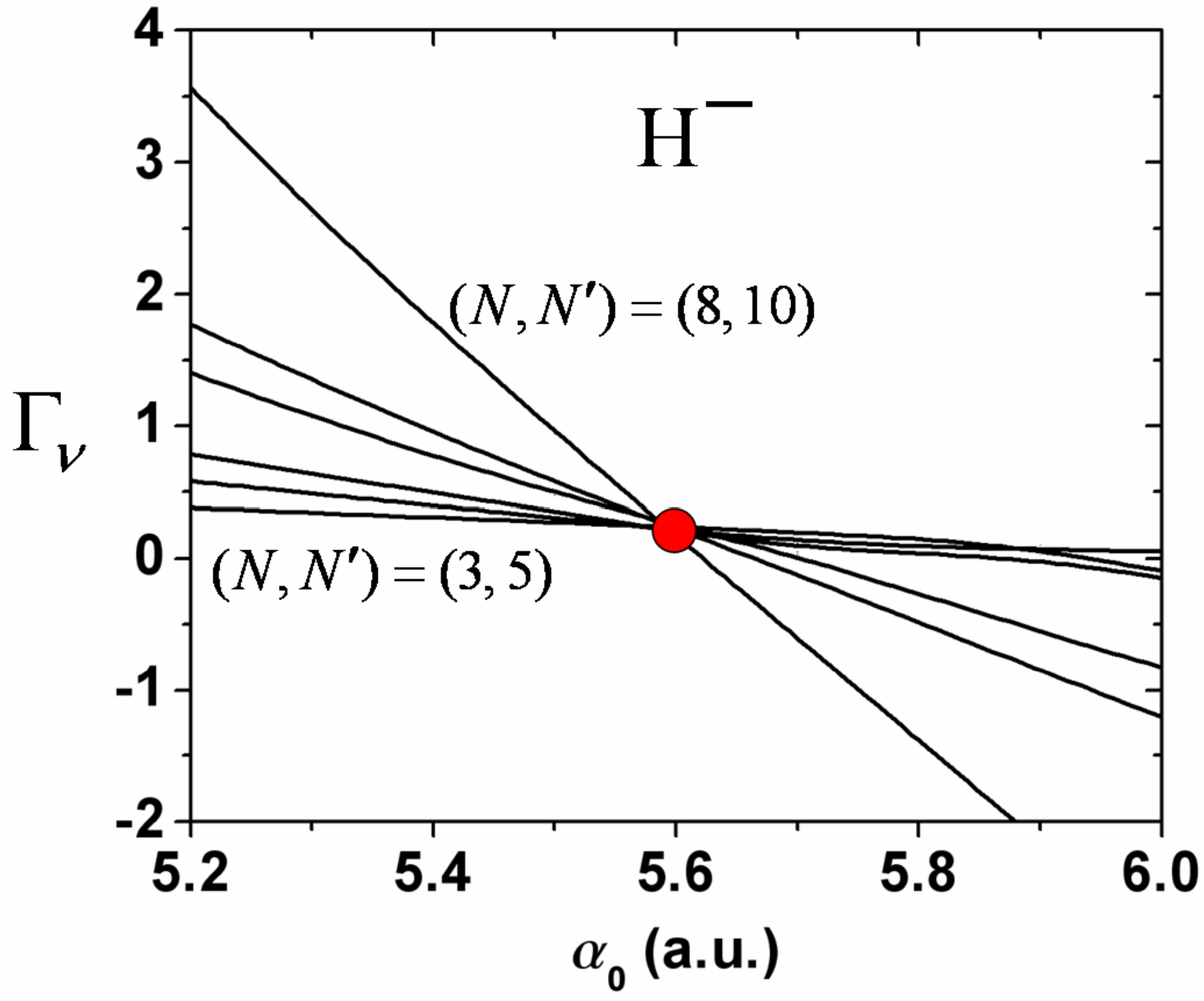
Journal of Chemical Physics, 128, 044307 (2008)

Finite Size Scaling

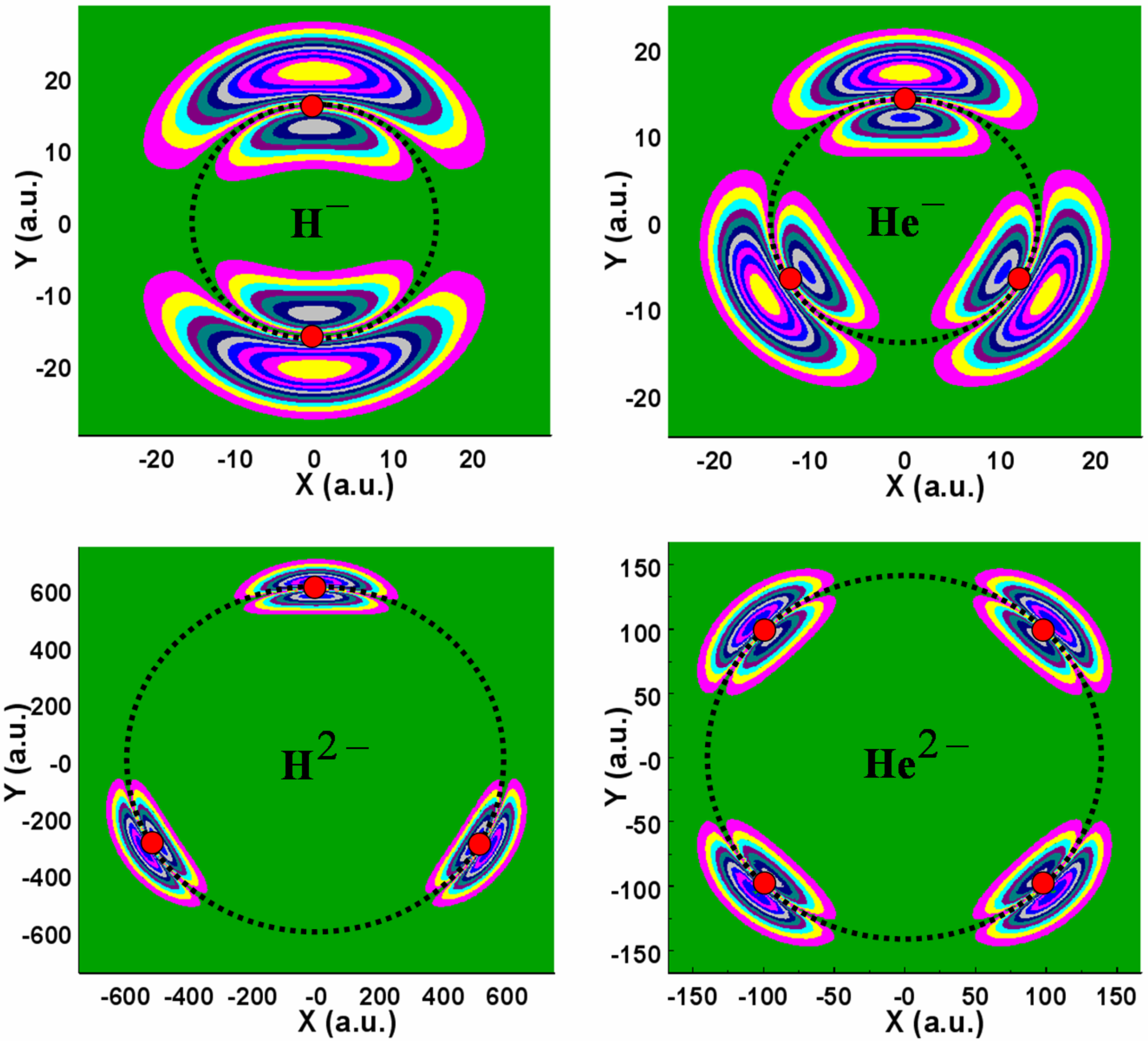
Stability of Atomic and Molecular Systems In Superintense Laser Fields

Journal of Chemical Physics, 127 094301 (2007).





H^-
$(N, N') = (8, 10)$
$(N, N') = (3, 5)$
Γ_ν
4
3
2
1
0
-1
-2
5.2
5.4
5.6
5.8
6.0
α_0 (a.u.)

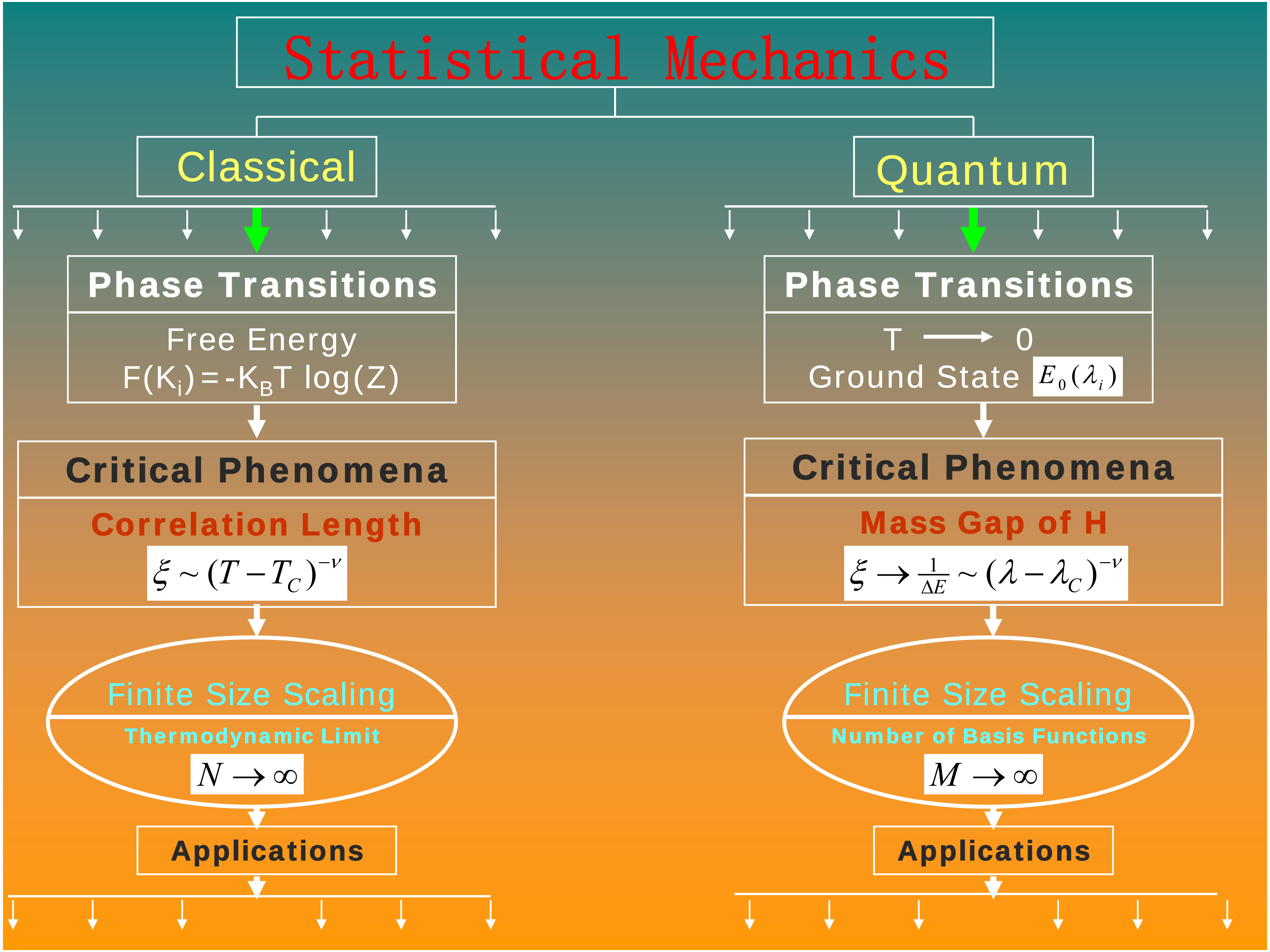


20
10
0
-10
-20
Y (a.u.)
H−
-20 -10 0 10 20
X (a.u.)
20
10
0
-10
-20
Y (a.u.)
He−
-20 -10 0 10 20
X (a.u.)
600
400
200
-0
-200
-400
-600
Y (a.u.)
H2−
-600 -400 -200 -0 200 400 600
X (a.u.)
150
100
50
-0
-50
-100
-150
Y (a.u.)
He2−
-150 -100 -50 -0 50 100 150
X (a.u.)

Critical parameters for stability of atomic anions in super-intense laser fields

Quantity	D	Polz.[a]	H^-	H^{2-}	He^-	He^{2-}
α_0^{crit}(a.u.)	3	L	6	170	11	82
		C	6	250	4.3	51
	∞	L	3	181	3	59
		C	2.6	300	1.3	45
I^{crit} $(10^{16}\ \frac{W}{cm^2})$	3	L	0.14	120	0.48	27
		C	0.14	250	0.074	10
	∞	L	0.036	130	0.06	14
		C	0.027	360	0.0068	8.1
α_0^{max}(a.u.)	3	L	17	400	26	180
		C	16	600	14	140
	∞	L	10	500	12	160
		C	10	834	6	130
I^{max} $(10^{16}\ \frac{W}{cm^2})$	3	L	1.2	640	2. 7	130
		C	1.0	1400	0.79	79
	∞	L	0.4	1000	0.58	100
		C	0.4	2800	0.14	68
DE (eV)	3	L	1.1	0.026	1.2	0.12
		C	0.37	0.0073	1.1	0.078
	∞	L	1.2	0.019	1.4	0.14
		C	0.46	0.0052	1.1	0.066

[a] L and C denote linear and circular polarization, respectively. Data pertain to $\omega = 5$eV.


Statistical Mechanics
Classical
Quantum
Phase Transitions
Free Energy
$F(K_i) = -K_B T \log(Z)$
Phase Transitions
$T \longrightarrow 0$
Ground State $E_0(\lambda_i)$
Critical Phenomena
Correlation Length
$\xi \sim (T - T_C)^{-\nu}$
Critical Phenomena
Mass Gap of H
$\xi \to \frac{1}{\Delta E} \sim (\lambda - \lambda_C)^{-\nu}$
Finite Size Scaling
Thermodynamic Limit
$N \to \infty$
Finite Size Scaling
Number of Basis Functions
$M \to \infty$
Applications
Applications

Future Work

Combining FSS with Ab Initio and DFT
(Winton Moy and Dr. Pablo Serra)

Combining FSS with Finite Element Methods
(Dr. Marcelo Carignano and Winton Moy)

New Classification of Chemical Reactions
(Jing Zhu)

FSS and Efimov Systems
(Kangjun Seo, Qi Wei and Dr. Serra)

Stability of Matter in Superintese Laser Fields
(Prof. Dudley Herschbach and Qi Wei)

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