Finite Size Scaling and Stability of Atomic and Molecular Systems in Superintense laser fields

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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

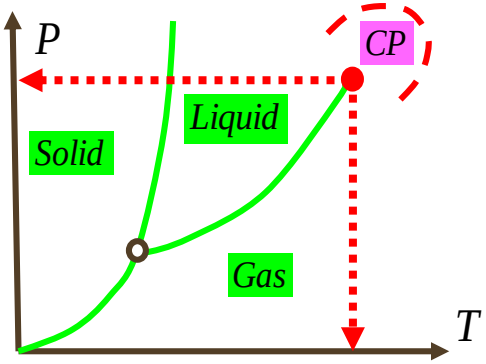
(3) Stability of Matter:
- (a) Atoms
- (b) Molecules
- (c) Quantum Dots

(4) Stabilization in Superintense Laser Fields

(5) Future Work: Open Problems

Phase Transitions

- Classical: Classical phase transitions are driven by thermal energy fluctuations

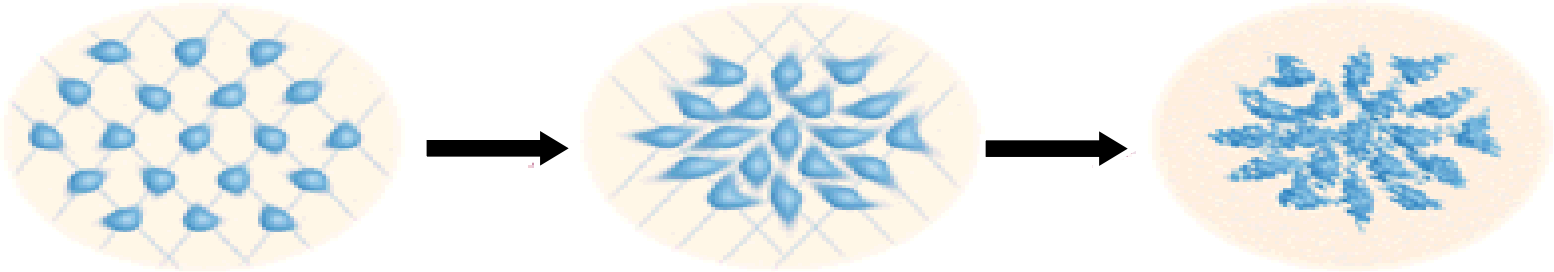


Like the melting of an ice cube:

$$\text{Solid} \rightarrow \text{Liquid} \rightarrow \text{Gas}$$

- Quantum: Quantum phase transitions, at T=0, are driven by the Heisenberg uncertainty principle

Like the melting of a Wigner crystal: Two dimensional electron layer trapped in a quantum well



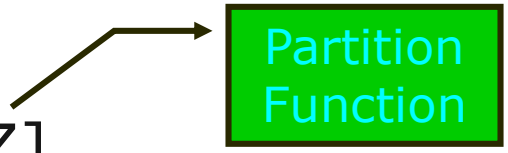
Quantum Phase Transitions

Transitions that take place at the absolute zero of temperature, T=0, where crossing the phase boundary means that the quantum ground state energy $E_0(\lambda)$, of the system changes in some fundamental way.

This is accomplished by changing some parameter in the Hamiltonian of the system $H_0(\lambda)$.

We shall identify any point of non-analyticity in the ground state energy $\lambda = \lambda_C$, as a quantum phase transition.

Phase Transition



Free energy: $f[K]=-k_B T \log[Z]$

Coupling Constants: $\{K_1, K_2; K_D\}$

As a function of [K], f[K] is analytic almost everywhere

Possible non-analyticities of f[K] are points ($D_S=0$), lines ($D_S=1$), planes ($D_S=2$), …

Regions of analyticity of f[K] are called phases

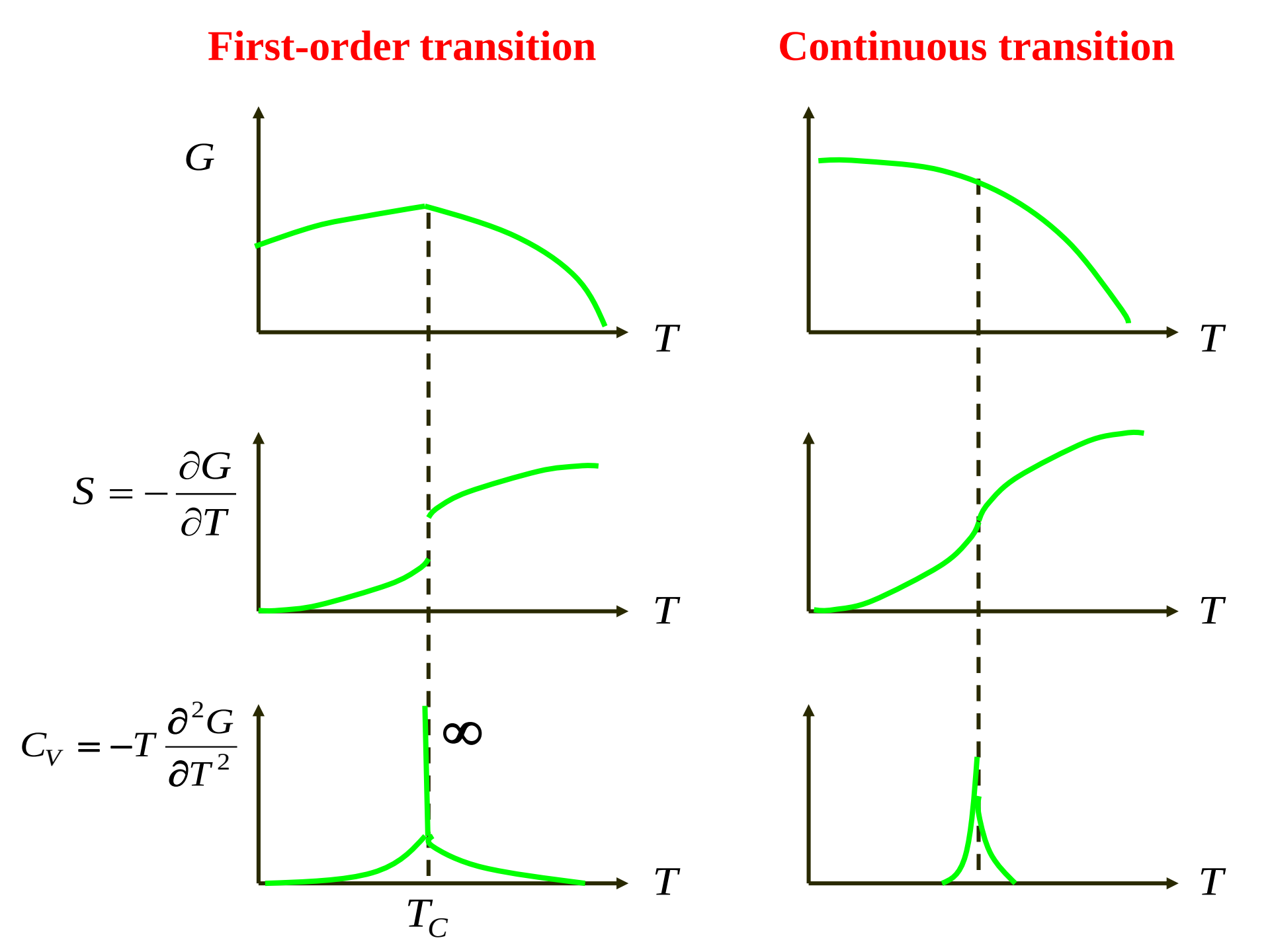
Phase Transitions

First-order:

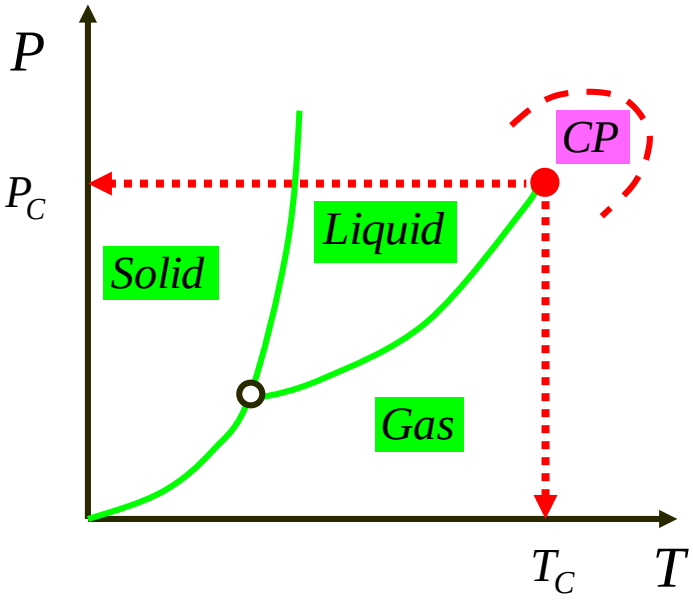
$\partial f / \partial K_i$ is discontinuous across a phase boundary

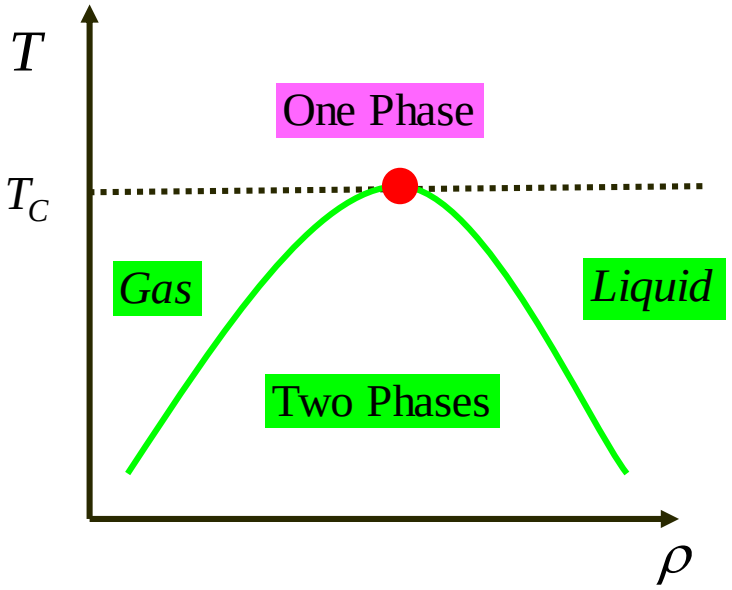
Continuous Phase Transition:

All $\partial f / \partial K_i$ are continuous across the phase boundary. But, second derivatives or higher derivatives are discontinuous or divergent


First-order transition
Continuous transition
G
T
$S = -\frac{\partial G}{\partial T}$
$C_V = -T\frac{\partial^2 G}{\partial T^2}$
∞
T_C

Phase Transitions





Order Parameter → $|\rho_+ - \rho_-| \propto |T - T_C|^{\beta}$ ← Critical Exponent

$\beta = 0.327$

Critical Exponents

The critical exponents describe the nature of the singularities in various measurable quantities at the critical point $[\alpha, \beta, \gamma, \delta, \eta, \nu]$

In the limit $T \to T_C$

- Heat Capacity: $C \sim |T - T_C|^{-\alpha}$
- Order Parameter: $M \sim |T - T_C|^{\beta}$
- Susceptibility: $\chi \sim |T - T_C|^{-\gamma}$
- Equation of State: $M \sim H^{1/\delta}$
- Correlation Length: $\xi \sim |T - T_C|^{-\nu}$

Scaling Laws:

- Fisher: $\gamma = \nu(2 - \eta)$
- Rushbrooke: $\alpha + 2\beta + \gamma = 2$
- Widom: $\gamma = \beta(\delta - 1)$
- Josephson: $\nu d = 2 - \alpha$

Universality Classes

Near a second-order phase transition macroscopic quantities show a universal scaling behavior that is characterized by critical exponents that depend only on general properties of the system, such as

its dimensionality,
symmetry of the order parameter, or
range of interaction.

Accordingly, phase transitions are classified in terms of universality classes.

Critical Exponents

$[\alpha, \beta, \gamma, \delta, \eta, \nu]$

Exponent	TH	EXPT	MFT	ISING2	ISING3	HEIS3
α		0-0.14	0	0	0.12	-0.14
β		0.32-0.39	½	1/8	0.31	0.3
γ		1.3-1.4	1	7/4	1.25	1.4
δ		4-5	3	15	5	
ν		0.6-0.7	½	1	0.64	0.7
η		0.05	0	¼	0.05	0.04
$\alpha+2\beta+\gamma$	2	2.00 ± 0.01	2	2	2	2
$(\beta\delta-\gamma)/\beta$	1	0.93 ± 0.08	1	1	1	
$(2-\eta)\nu/\gamma$	1	1.02 ± 0.05	1	1	1	1
$(2-\alpha)/\nu d$	1		4/d	1	1	1

TH. Theoretical values (from scaling laws); EXPT. Experimental values (from a variety of systems); MFT. Mean field theory; ISINGd. Ising model in d dimension; HEIS3. classical Heisenberg model. D=3

Kenneth G. Wilson (1982)

The Nobel Prize in Physics 1982

Kenneth G. Wilson

Cornell University

Renormalization Group

"for his theory for critical phenomena in connection with phase transitions"

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

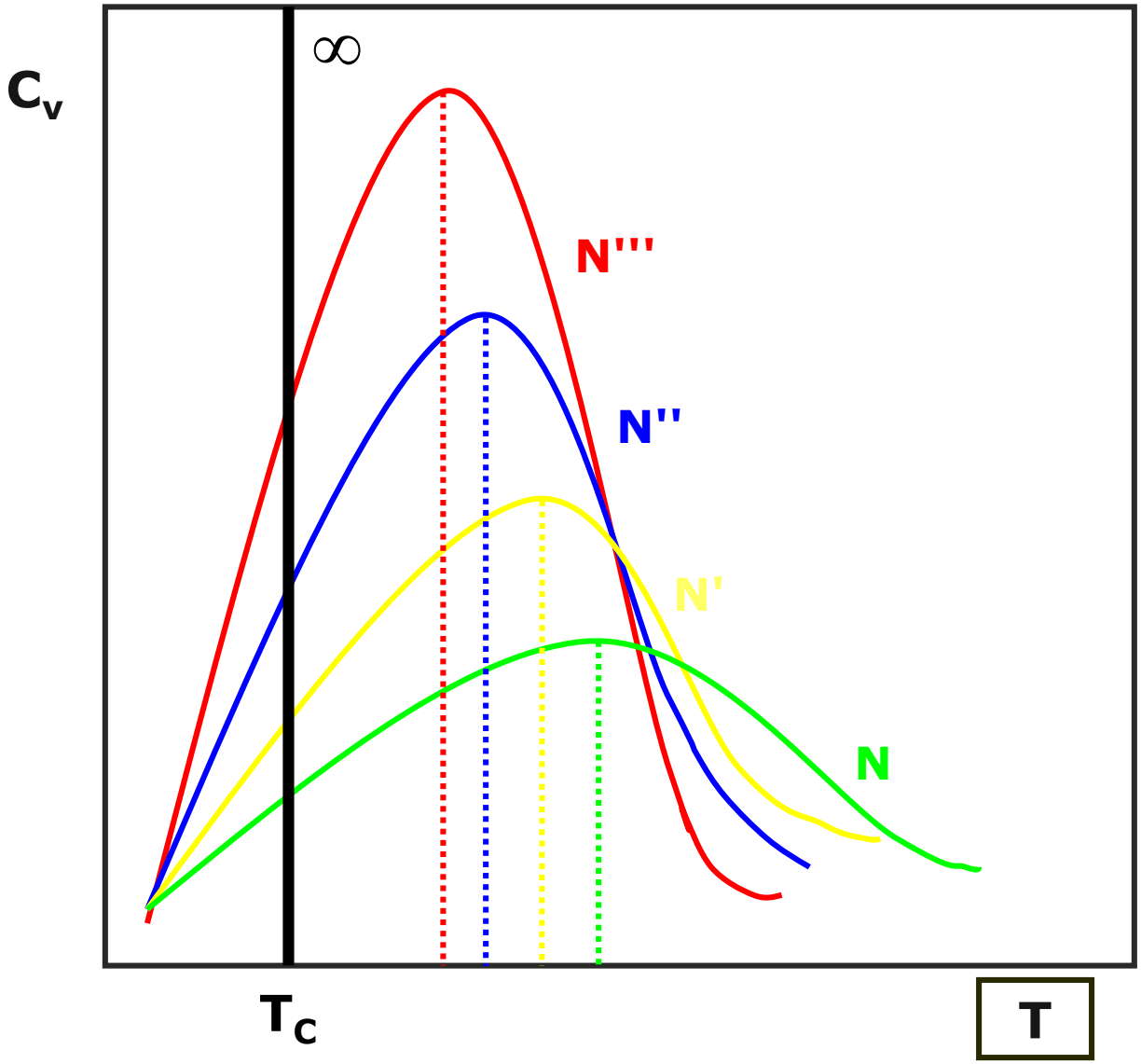
Importance

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)***

The Nobel Prize in Physics 1957

Finite-size effects in Statistical Mechanics



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 $K^{(q)}(\lambda)$ is the qth derivative of $K(\lambda)$, $K^{(q)}(\lambda)$ 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

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

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.

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

Nightingal e developed the phenomenol ogical renormaliz ation (PR) equation for finite systems of sizes N and N′ is given by

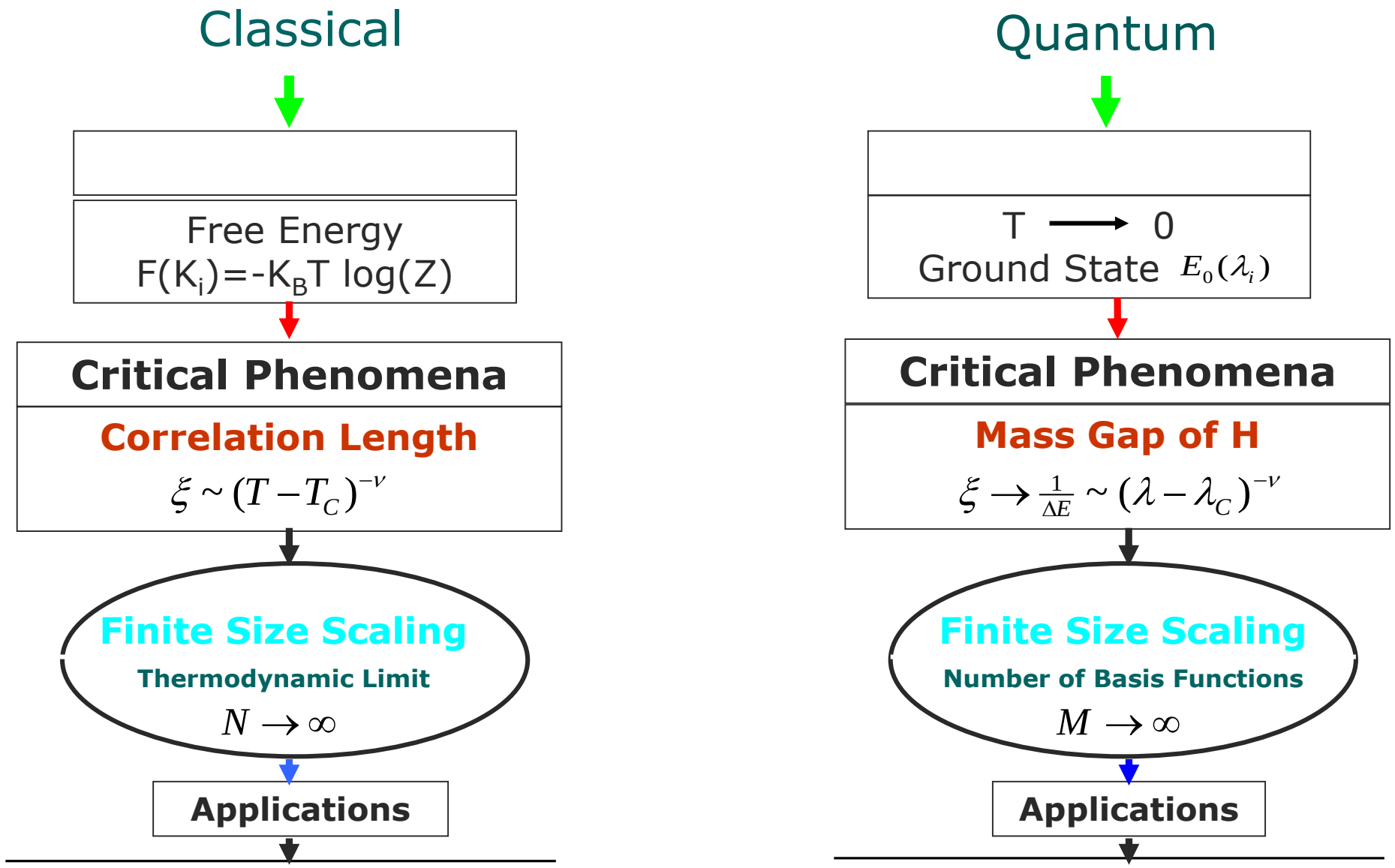
$$\frac{\xi_N(\lambda)}{N} = \frac{\xi_{N'}(\lambda')}{N'}$$

and has a fixed point at (N,N'). It is expected that the succession of points $\{\lambda^{(N,N')}\}$ in the limit of infinite sizes to converge to the true λ_c.

Using the definition of the correlatio n length, then at the fixed point can be written as

$$\left(\frac{E_1^{(N)}(\lambda^{(N,N')})}{E_0^{(N)}(\lambda^{(N,N')})}\right)^N = \left(\frac{E_1^{(N')}(\lambda^{(N,N')})}{E_0^{(N')}(\lambda^{(N,N')})}\right)^{N'}$$

Statistical Mechanics



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

In order to apply FSS to quantum mechanics problems, let us consider the following Hamiltonian of the form

$$H = H_0 + V_\lambda$$

where H_0 is λ-independent and V_λ is λ-dependent term

For a given complete orthonormal λ-independent basis set $\{\phi_n\}$, the ground state eigenfunction has the following expansion

$$\psi_\lambda = \sum_n a_n(\lambda)\phi_n$$

The Nth-order approximation for the energies are given by the eigenvalues $\{\Lambda_i^{(N)}\}$ of the matrix $H^{(N)}$,

$$E_\lambda^{(N)} = \min_{\{i\}} \left\{ \Lambda_i^{(N)} \right\}$$

The corresponding eigenfunction are given by

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

The expectation value of any operator O

$$\langle O \rangle_\lambda^{(N)} = \sum_{n,m}^{N} a_n^{(N)}(\lambda)\, a_m^{(N)}(\lambda) O_{n,m}$$

The FSS ansatz

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

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

The curves intersect at the critical point

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

In order to obtain the critical exponent α for the energy

$$\frac{\alpha}{\nu} = \Delta_H(\lambda_C; N, N')$$

Hellmann-Feynman Theorem

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_\lambda = \left\langle \frac{\partial V_\lambda}{\partial \lambda} \right\rangle_\lambda$$

$O = \partial V_\lambda / \partial \lambda$ gives an equation for $(\alpha - 1)/\nu$

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

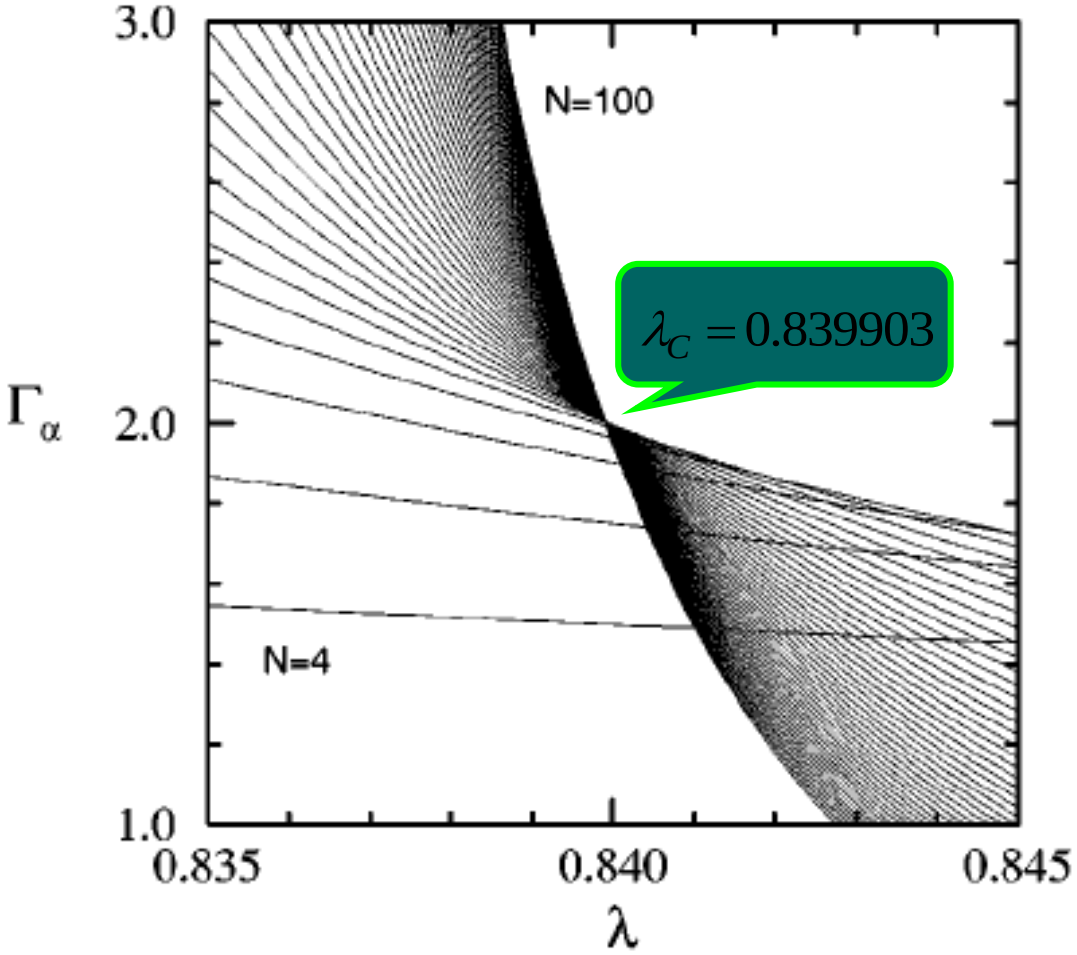
$$H(\lambda) = -\frac{1}{2}\nabla^2 - \lambda\frac{e^{-r}}{r}$$

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.

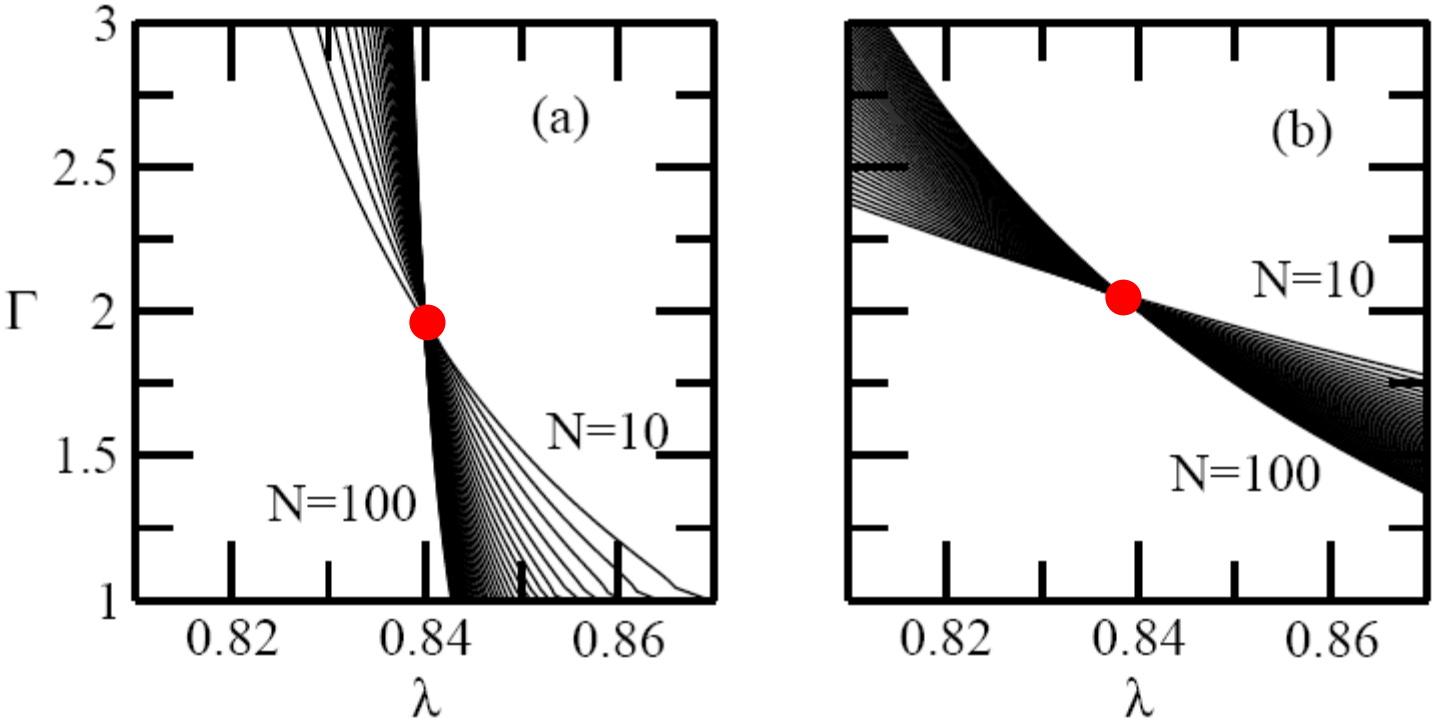
The basis-set is an over-complete set of Gaussian functions:

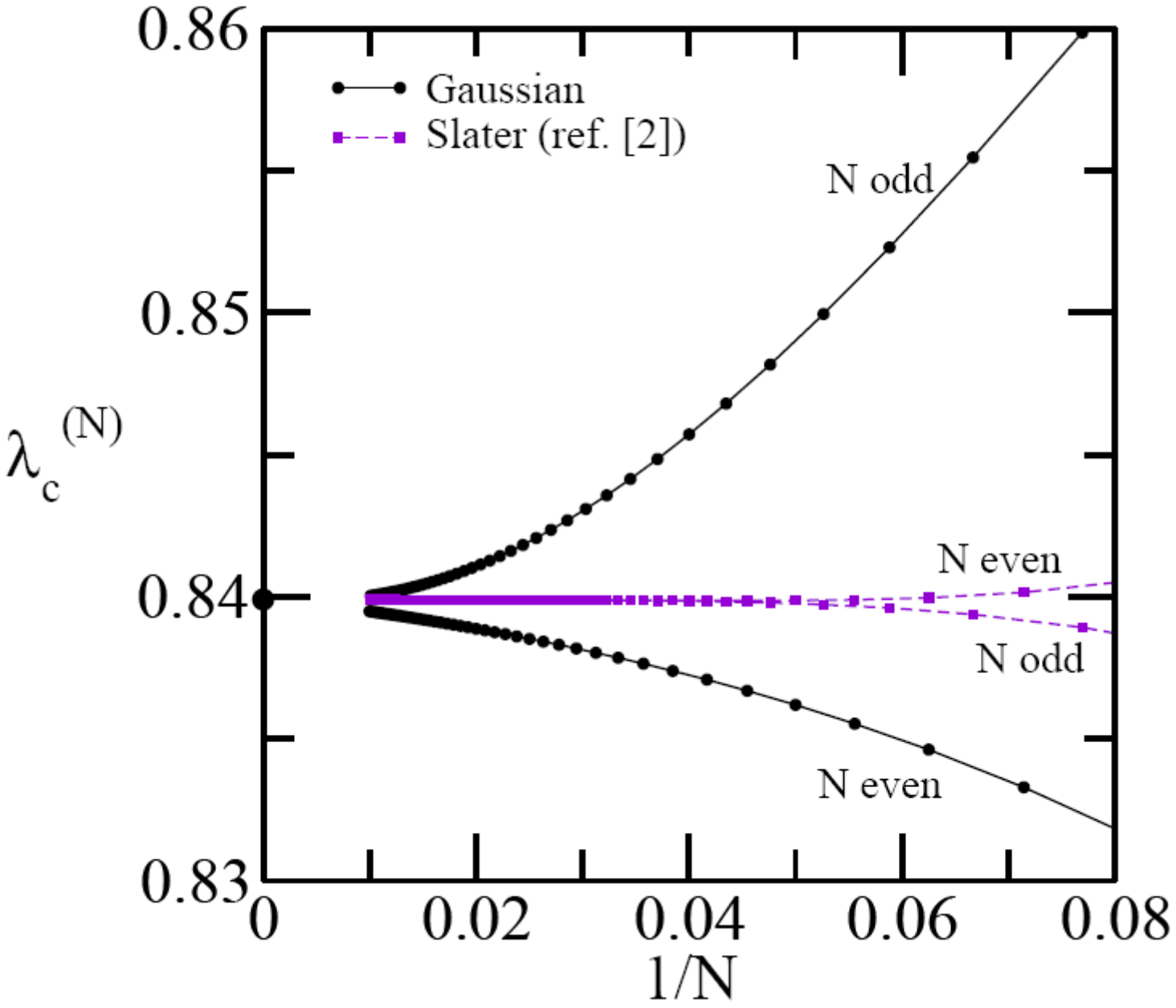
$$\phi_{i,j,k}(\beta;\vec{x}) = C_{ijk}\exp(-\beta r^2)x^i y^j z^k$$

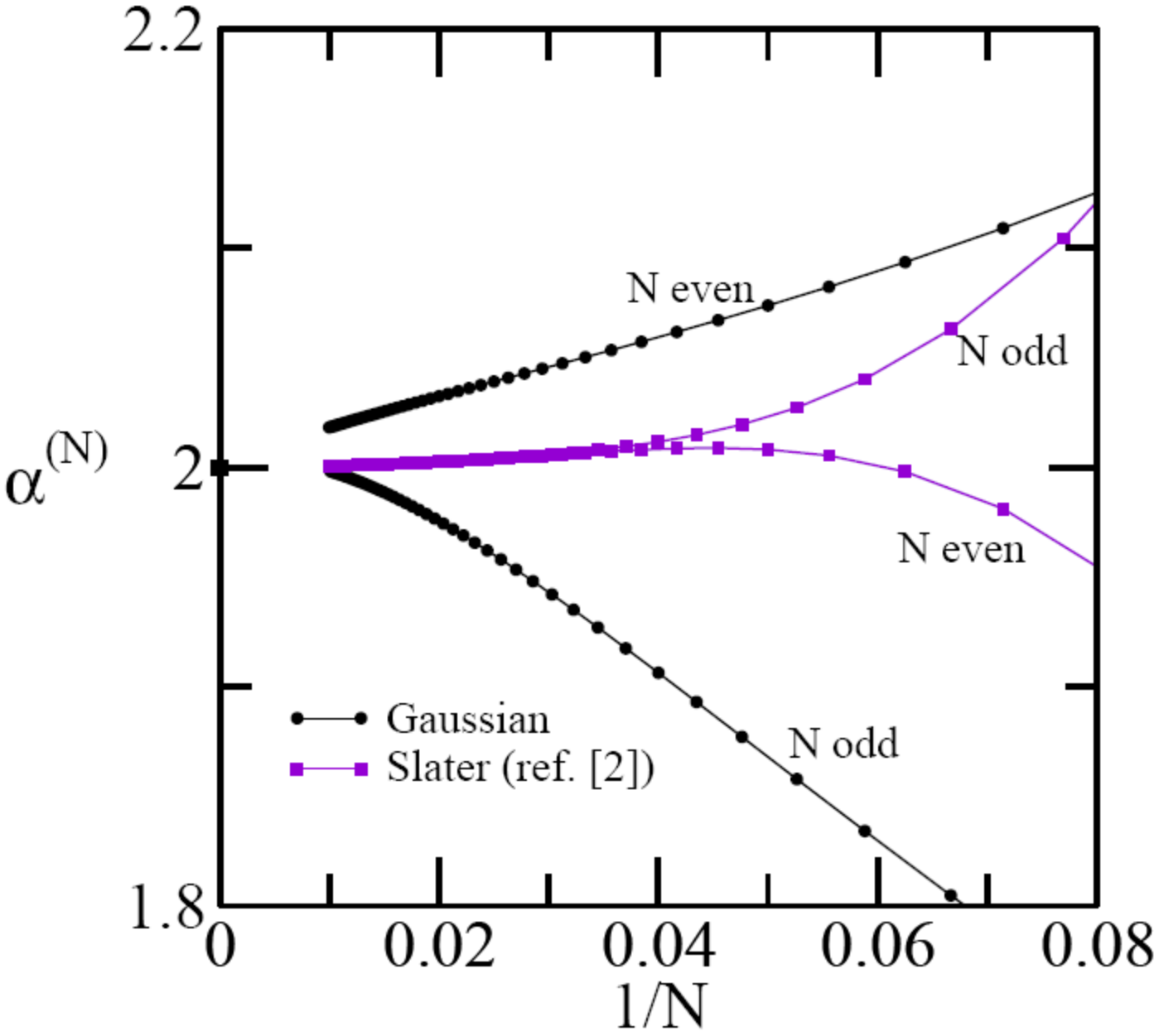
Where C_{ijk} are the normalization constants and βis a free parameter.

Gaussians

Slater




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


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

Finite Size Scaling
Data Collapse

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

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

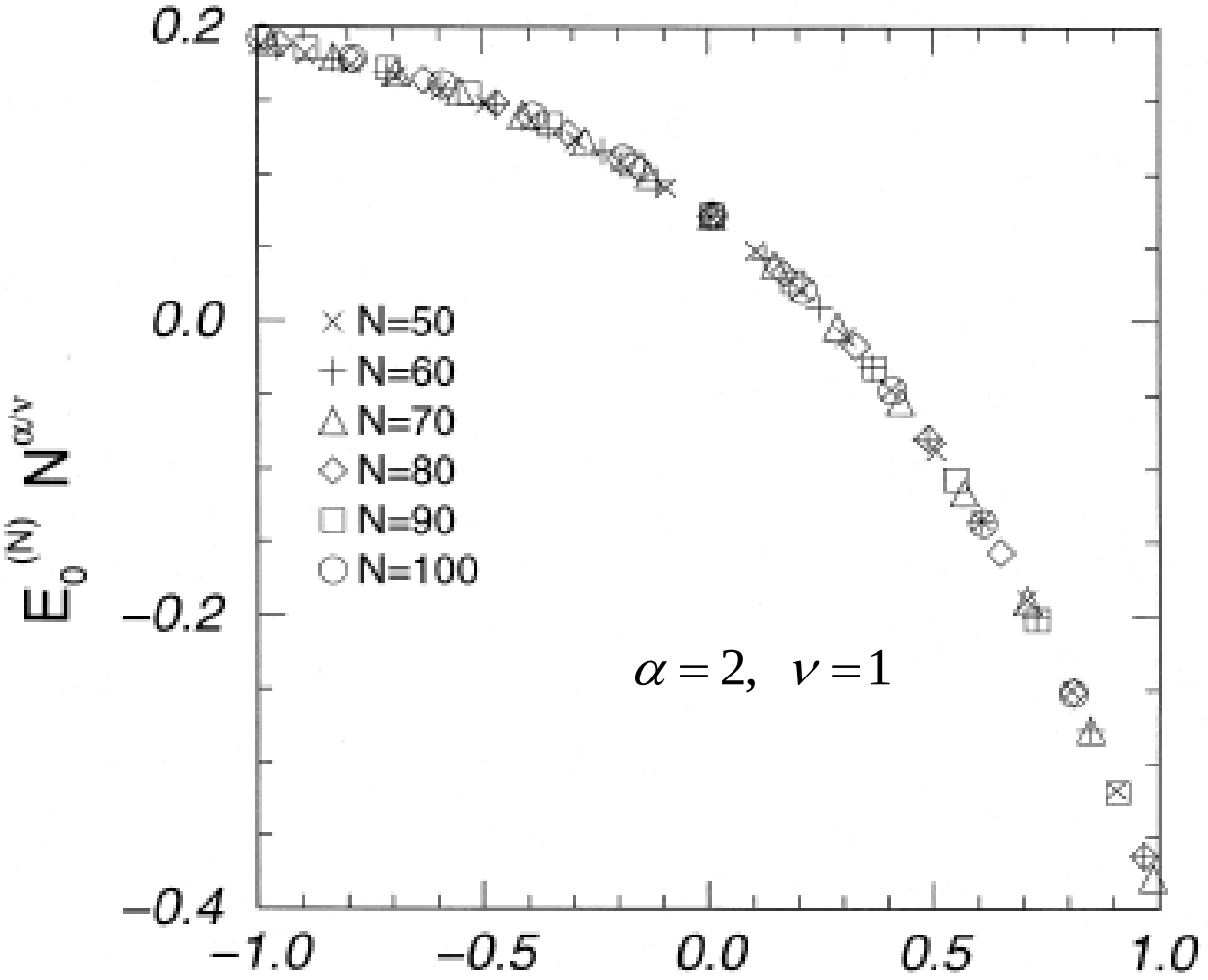
$$F(x) \underset{x \to 0}{\sim} x^{-\mu/\nu}$$

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

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

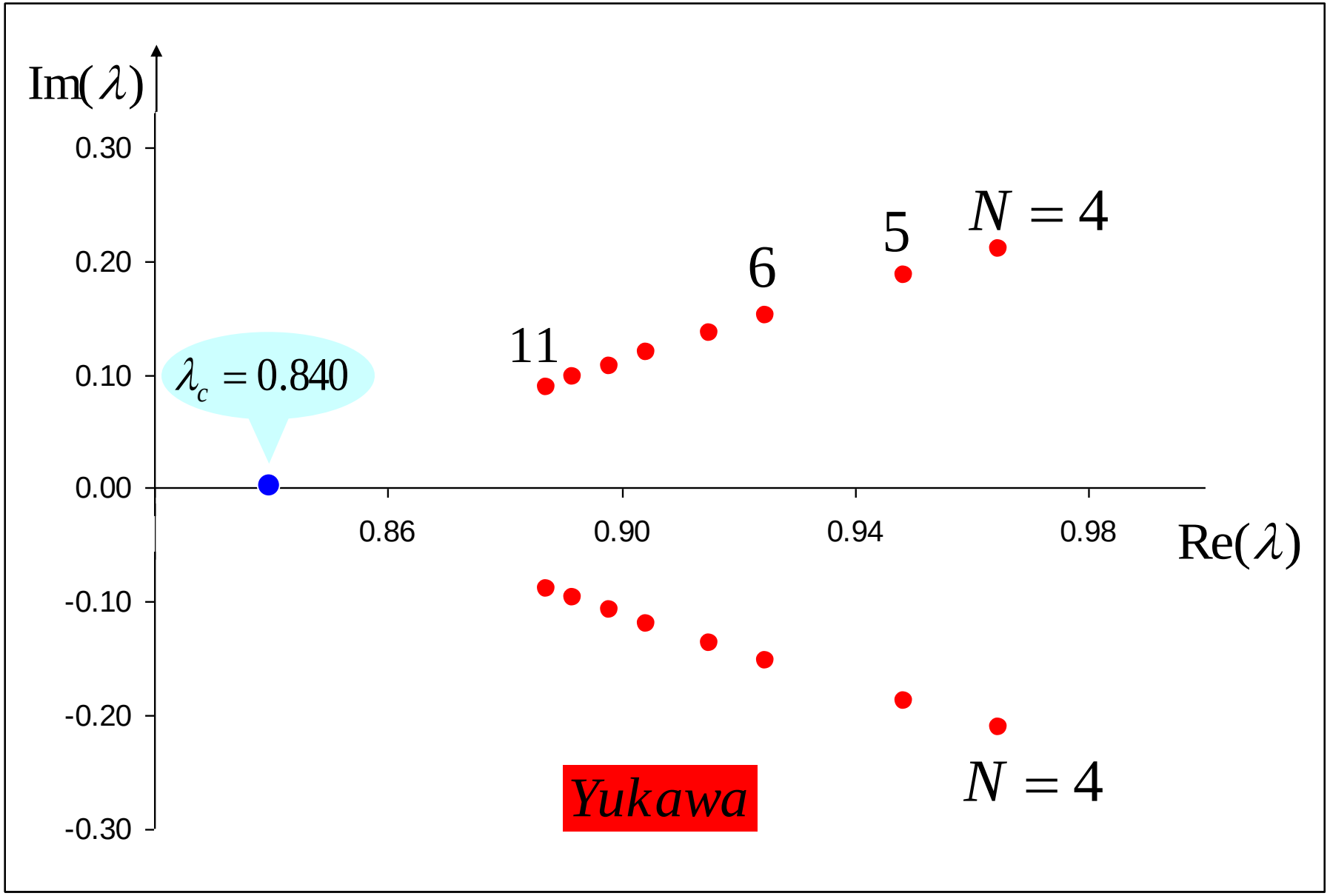
$$E_0 N^{\alpha/\nu} \sim G\left(N^{1/\nu}(\lambda - \lambda_C)\right)$$

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



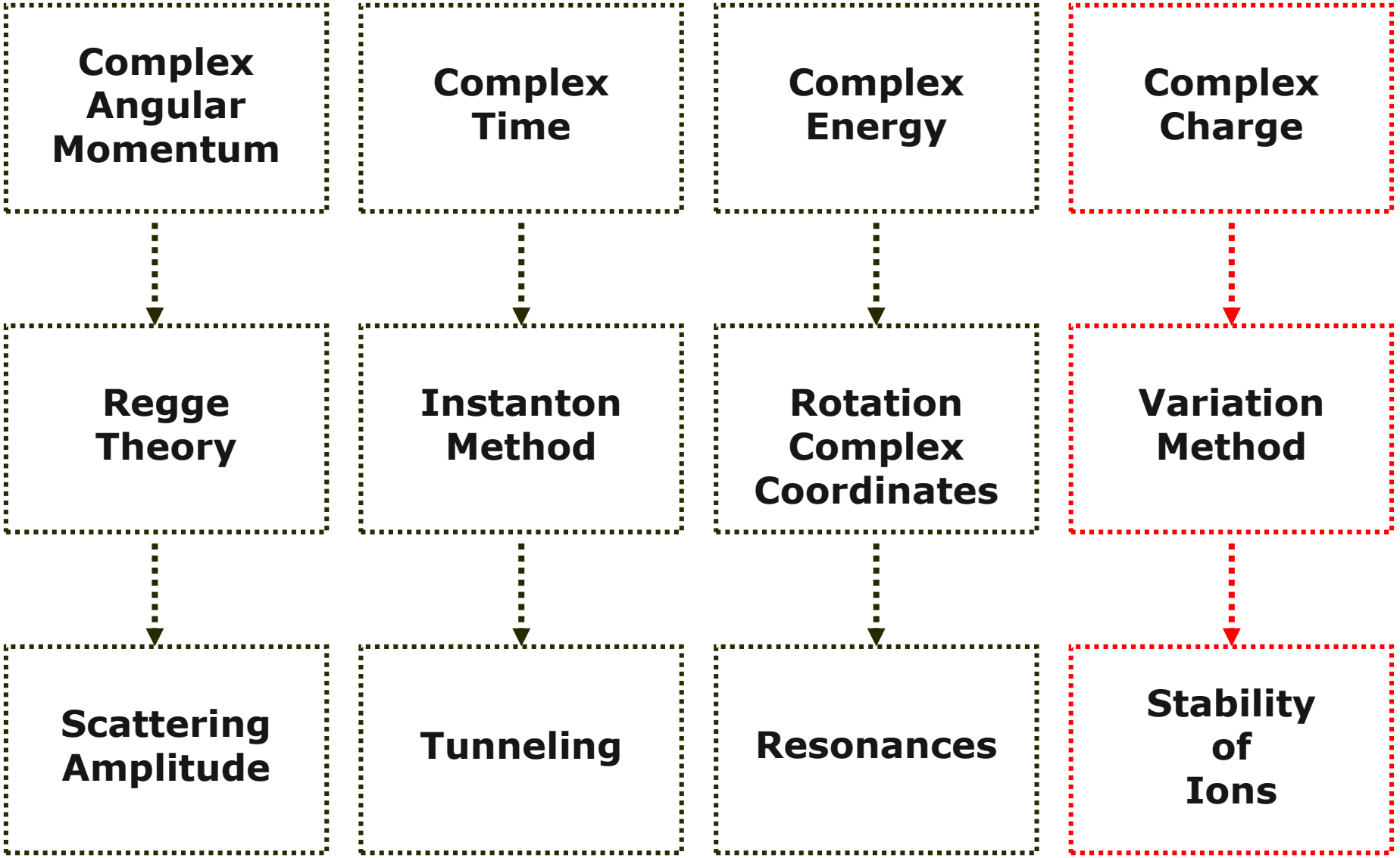
$(\lambda - \lambda_C) N^{1/\nu}$

Chem. Phys. Letters 319, 273 (2000)



Chem. Phys. Letters 423, 45 (2006)

Quantum Mechanics

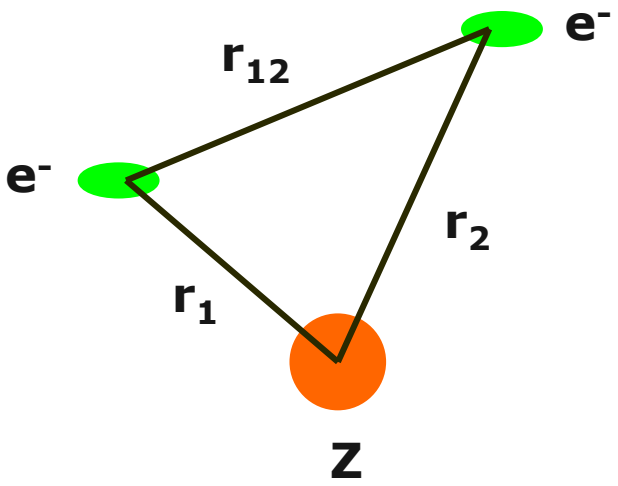


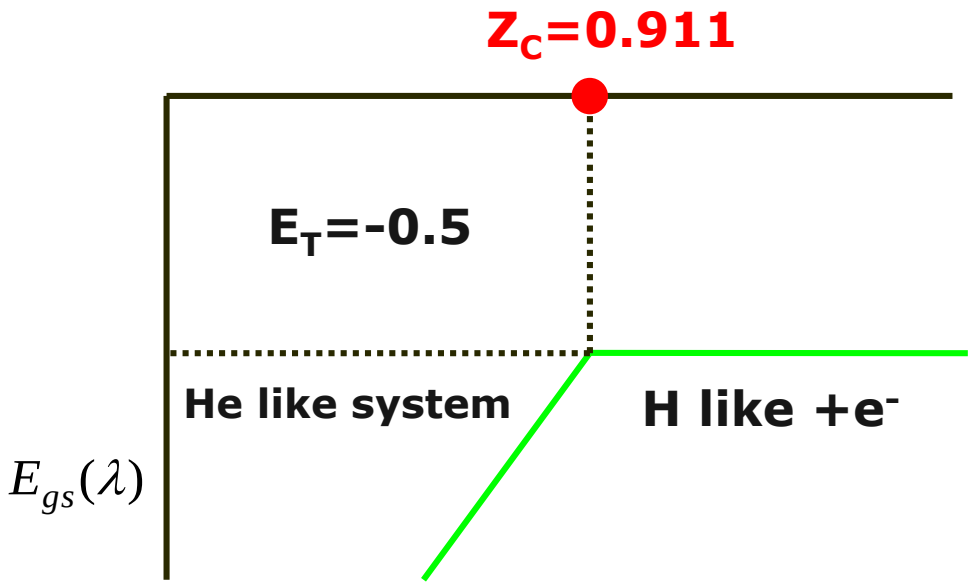
Two Electrons Atoms

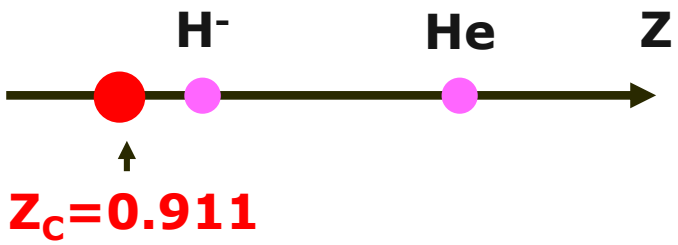
$$H(\lambda) = -\frac{1}{2}\nabla_1^{\,2} - \frac{1}{2}\nabla_2^{\,2} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}}$$

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

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







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:**

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

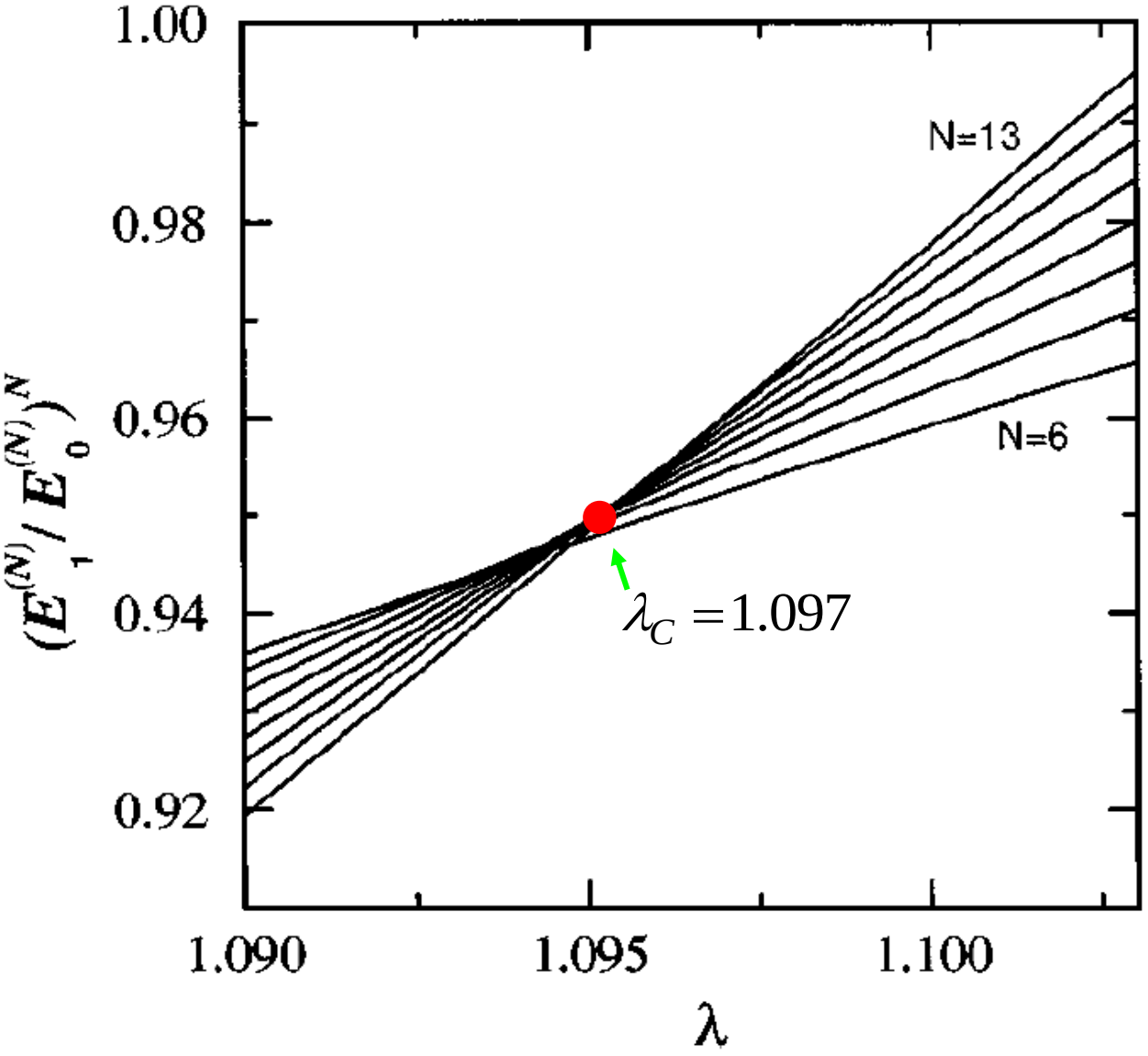
$$i + j + k \le N$$

- **Hamiltonian Matrix:**

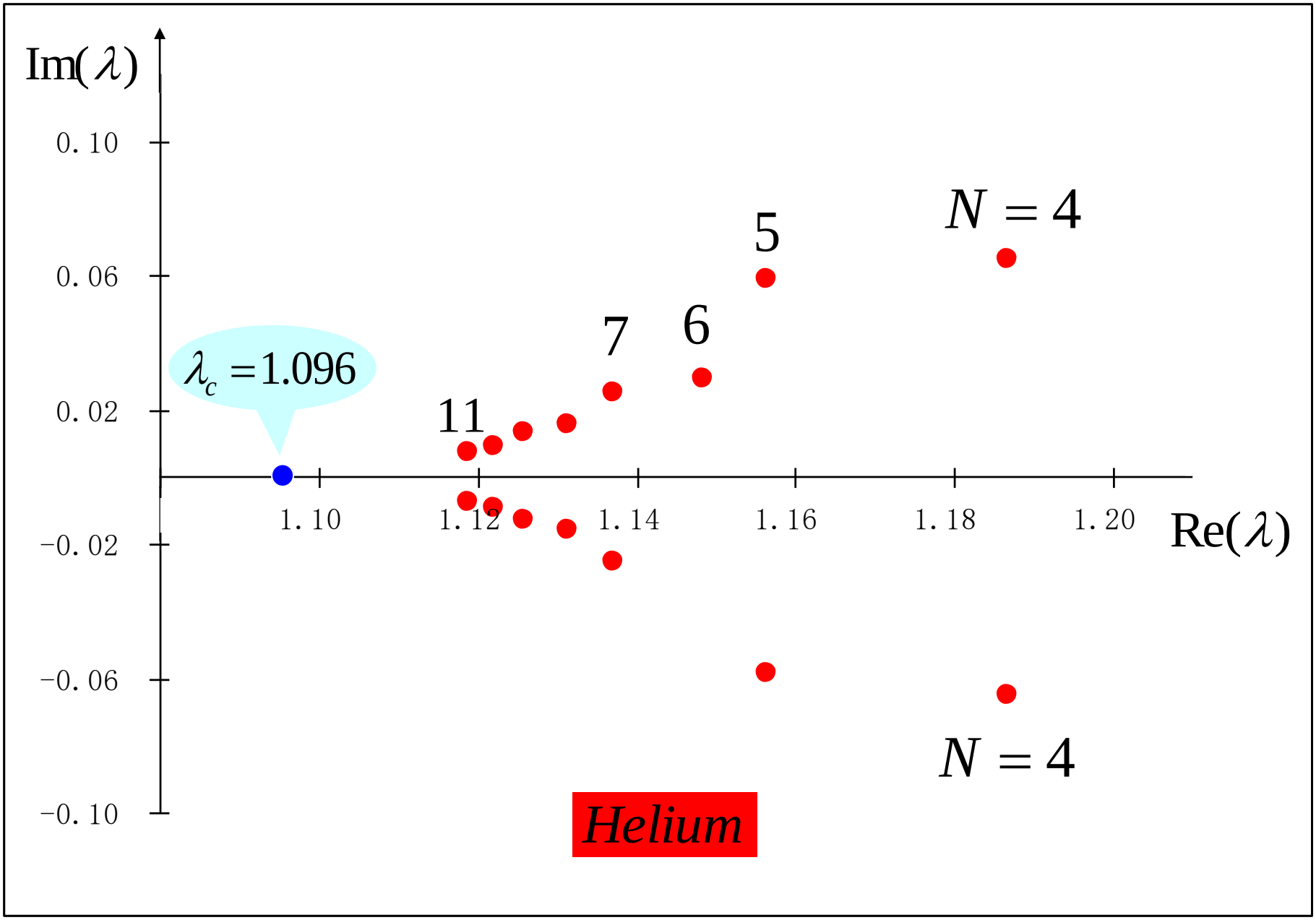
Leading Eigenvalue s, E_0, E_1

- **Renormalization Equation:**

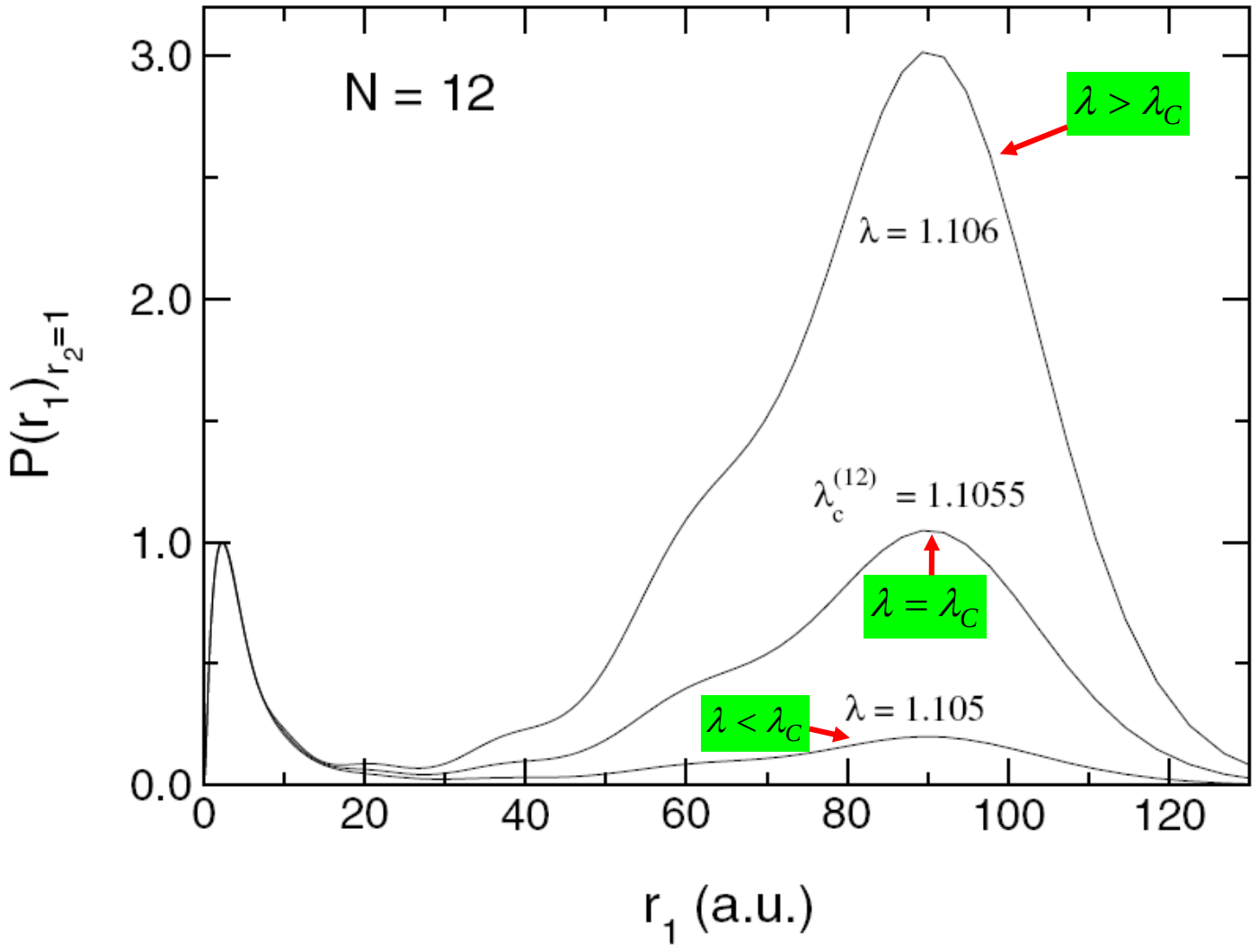
$$\left(\frac{E_1(N)}{E_0(N)} \right)^N = \left(\frac{E_1(N+1)}{E_0(N+1)} \right)^{N+1}$$



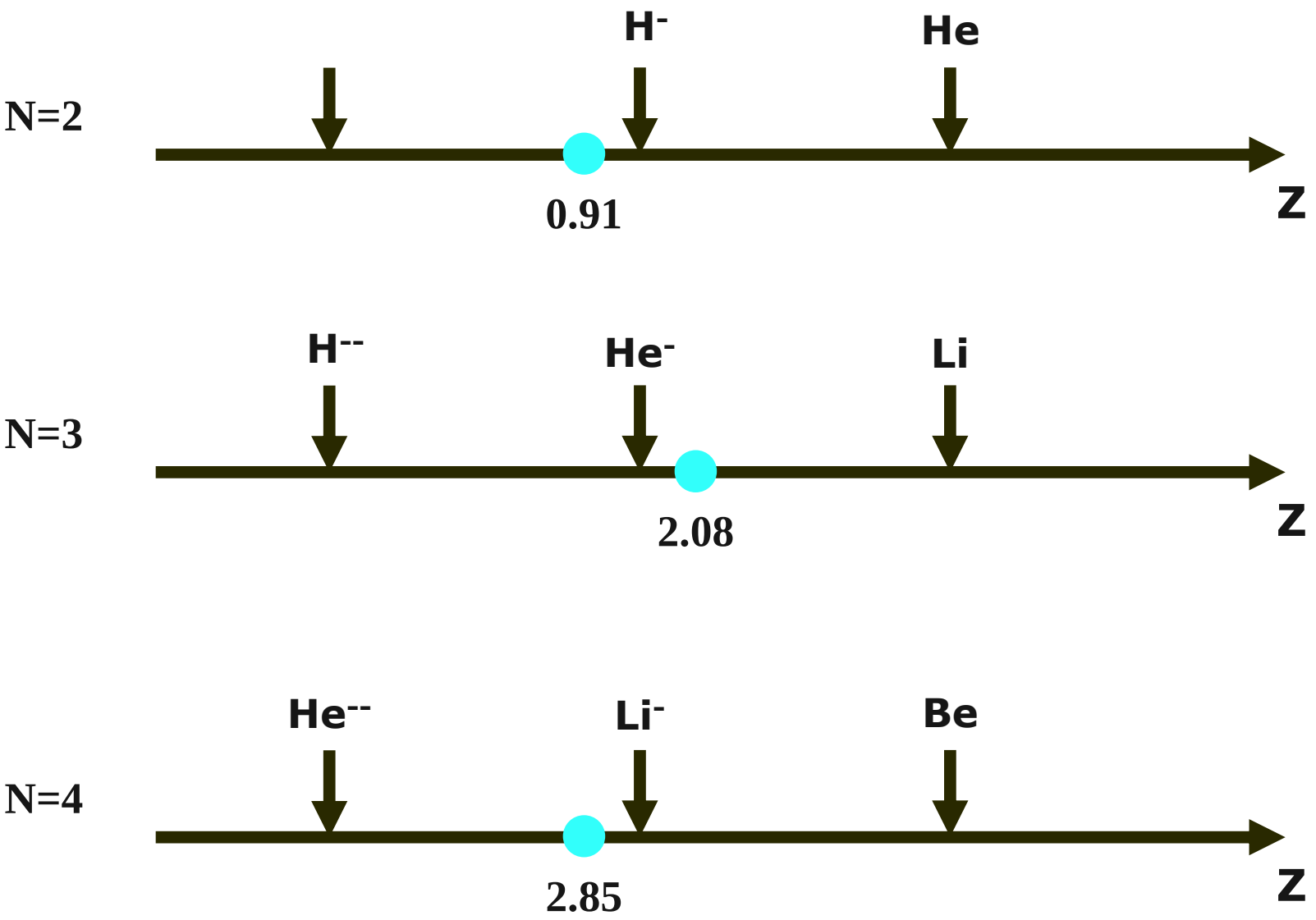
Phys. Rev. Letters 80, 5293 (1998)


Im(λ)
0. 10
0. 06
0. 02
−0. 02
−0. 06
−0. 10
λc =1.096
1. 10
1. 12
1. 14
1. 16
1. 18
1. 20
Re(λ)
11
7
6
5
N = 4
N = 4
Helium

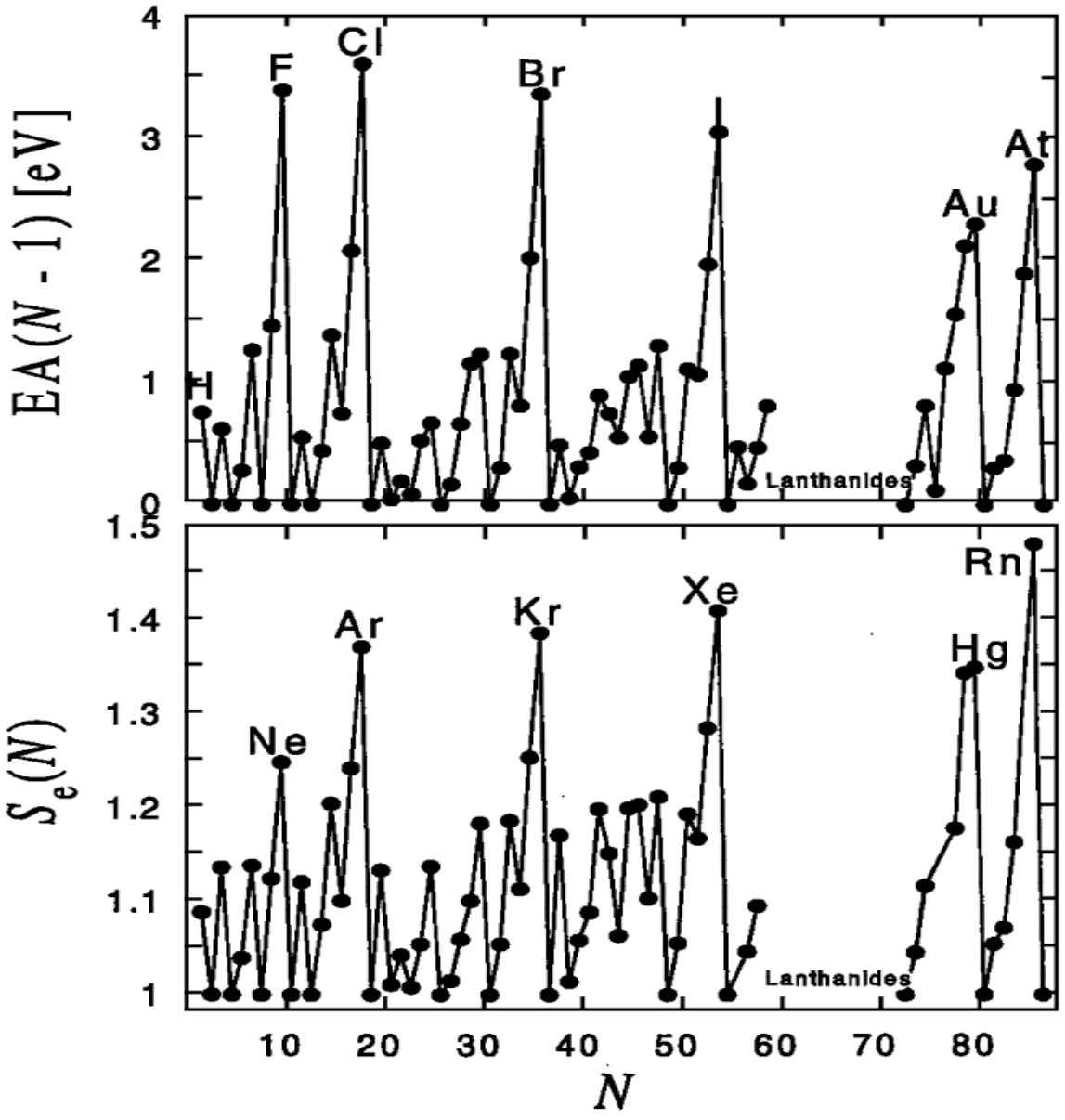
Conditional Probability



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

Model Potential for Spherical Molecular Dianions

From classical electrostatics, the electrostatic potential between an electron ($q = e$) and a dielectric sphere of radius R is given by

$$\varphi(\mathbf{r}) = \frac{q}{|\,\mathbf{r} - \mathbf{r}'\,|} - \sum_{l=0}^{\infty} q \frac{(\epsilon - 1)l}{(\epsilon + 1)l + 1} \frac{R^{2l+1}}{r^{l+1} r'^{l+1}} P_l(\cos\theta),$$

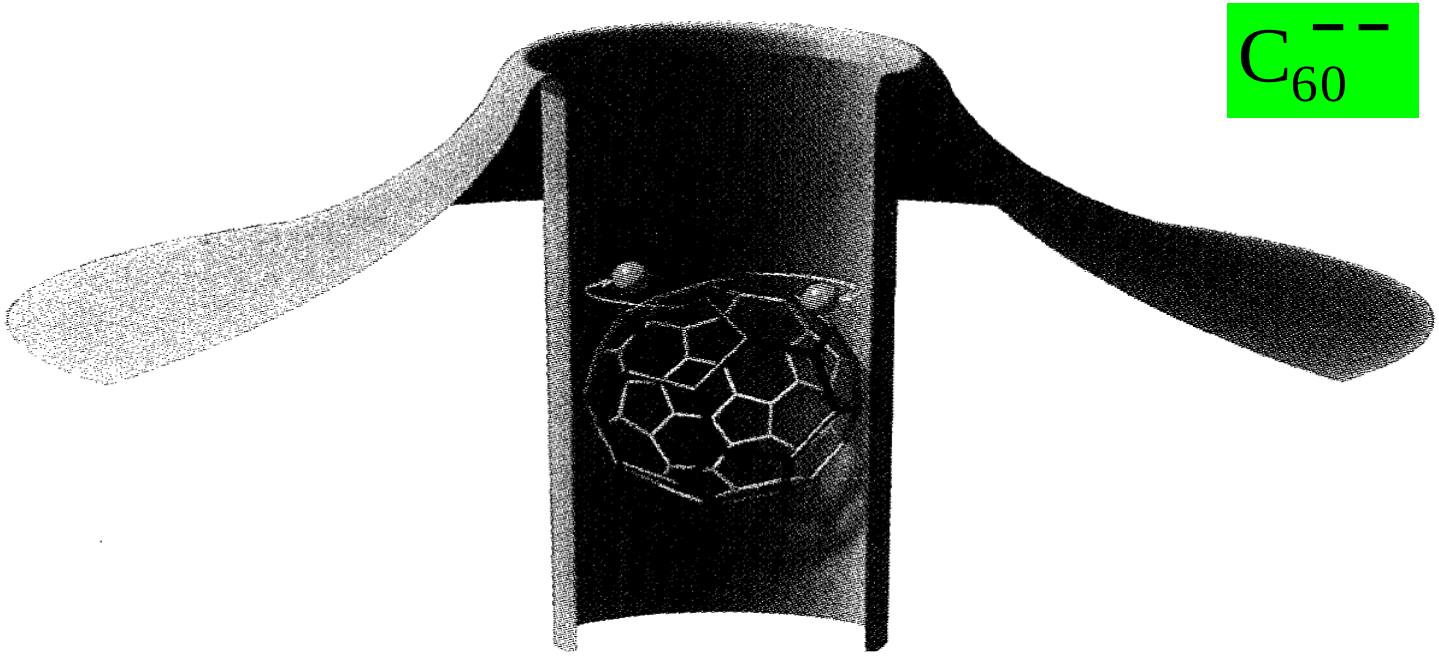
potential between an electron at a distance $r > R$ and a negatively singly-charged sphere can be obtained using the method of images

$$V(r) = -V_0 \qquad r < R,$$

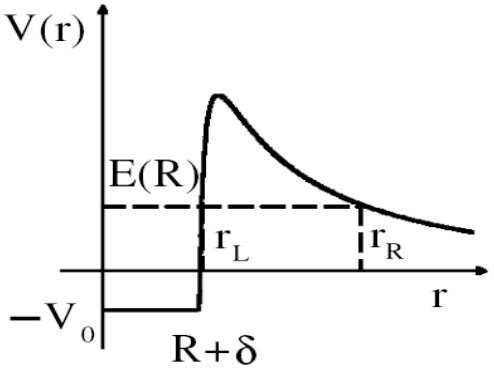
$$V(r) = -\frac{(\epsilon - 1)R^3}{2\,(\epsilon + 2)r^2(r^2 - R^2)} + \frac{1}{r} + \frac{l(l+1)}{2r^2} \qquad r > R,$$

where the constant $-V_0$ is an average attractive field inside the sphere.

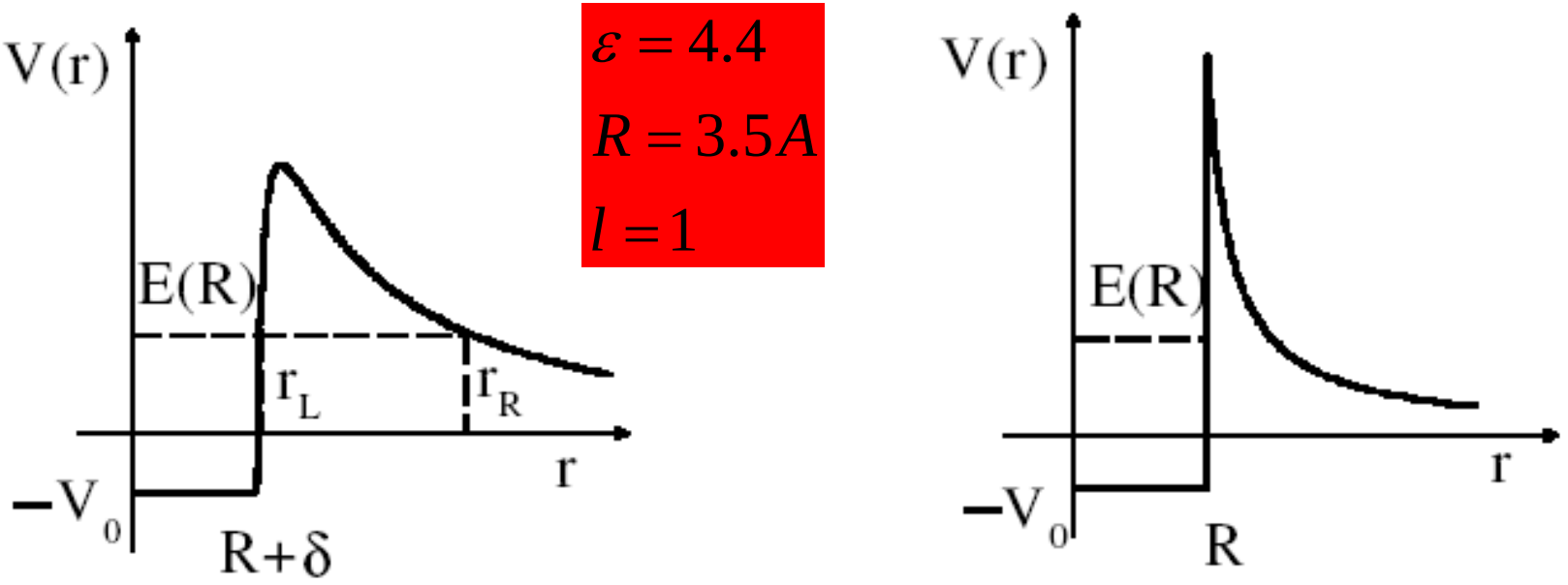
Stability of Spherical Carbon Cluster Dianions



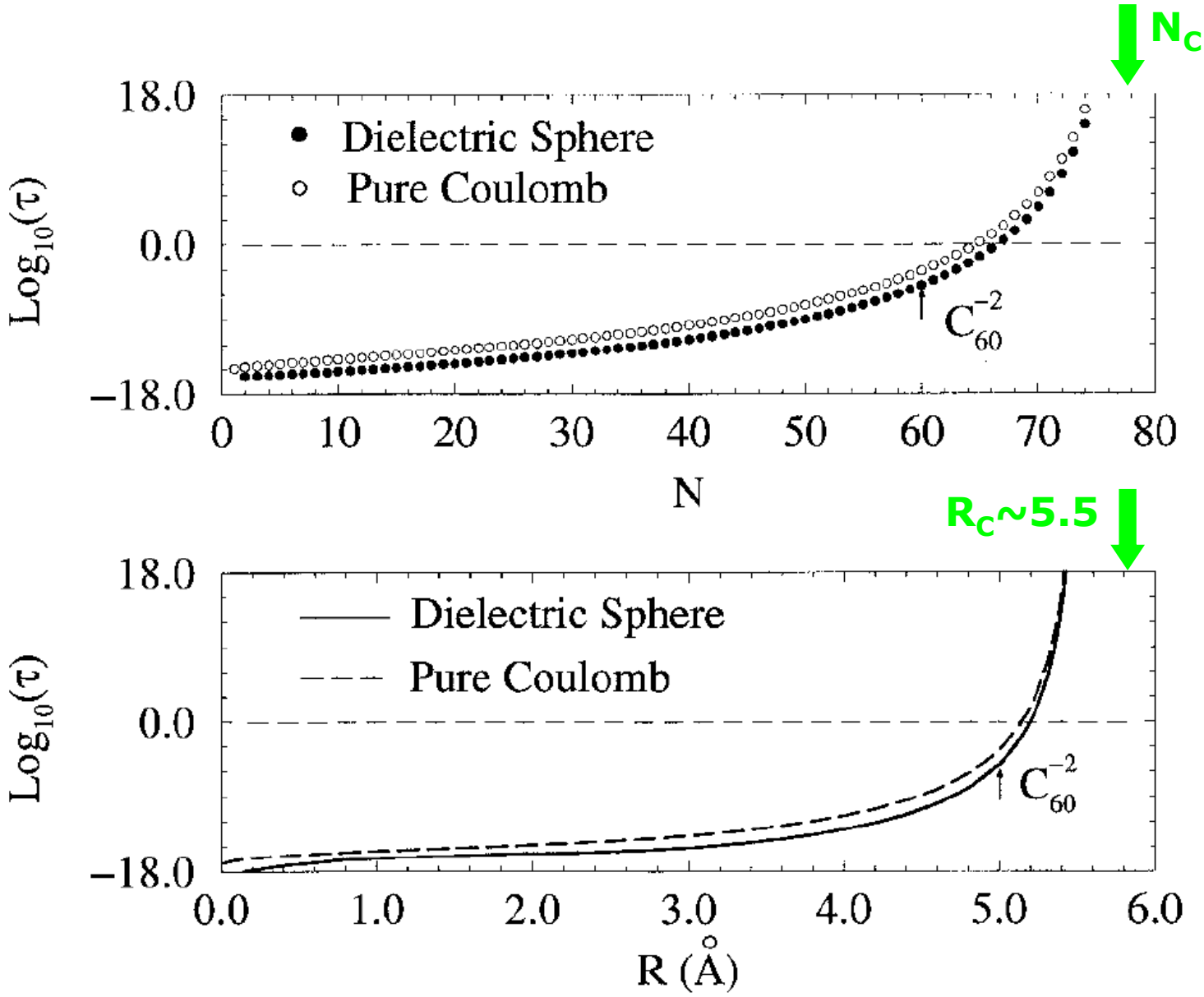
C_{60}^{--}



The interaction potential of an electron at a distance from a singly charged negative sphere of radius R and dielectric constant ε



C_{60}^{2-} Interaction potential $V(r)$ of an electron at distance r from a singly negative sphere of radius R (left) compared with a pure Coulomb repulsive potential (right).

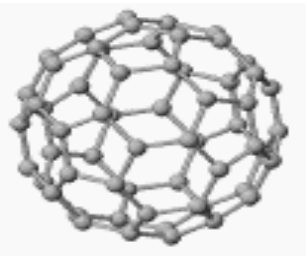


$\tau(C_{60}^{-2}) = 1ms \sim 0.1s$

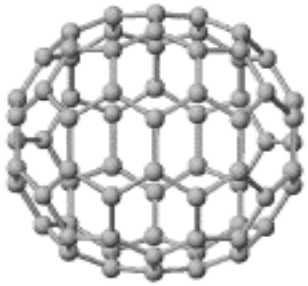
Molecular Physics 100, 475 (2002)

Stability of Dianions of Fullerenes

EA1 = + 2.65 eV
EA2 = - 0.3 eV



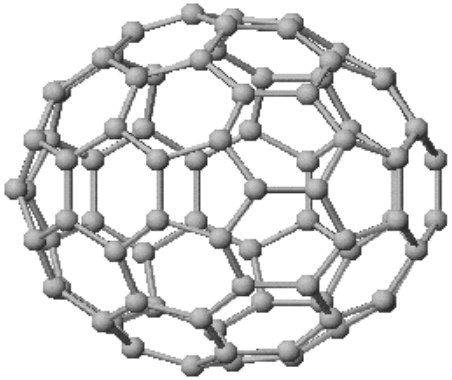
C_{60}^{-}



R_c = 5.6 A

C_{79}^{--}

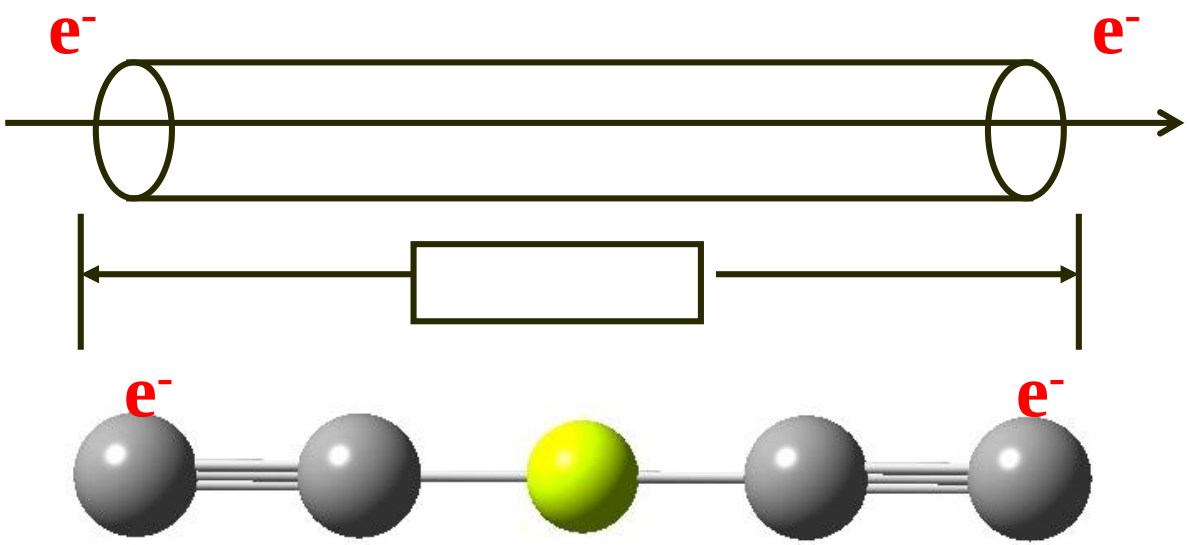
EA1 = + 3.14 eV
EA2 = + 0.44 eV



C_{84}^{--}

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

Stability of Linear Dianions

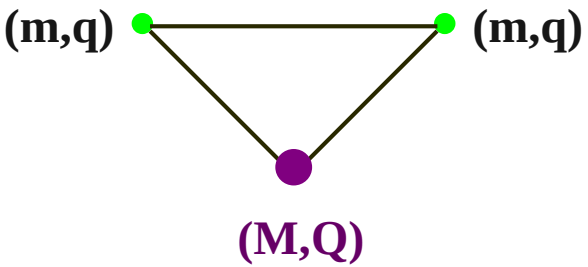


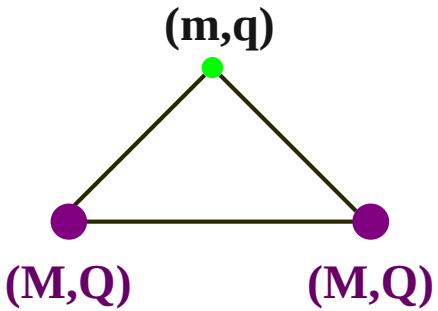
$^{-}C \equiv C - Be - C \equiv C^{-}$ $^{1}\sum_{g}^{+}$

BeC_4^{--}

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

Phase Transitions and Stability of Three Body Coulomb Systems





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

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

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

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

$$r \to fr$$

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

$$f = u|Qq|$$

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

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

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

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

Positronium Negative Ion: Molecule or Atom?

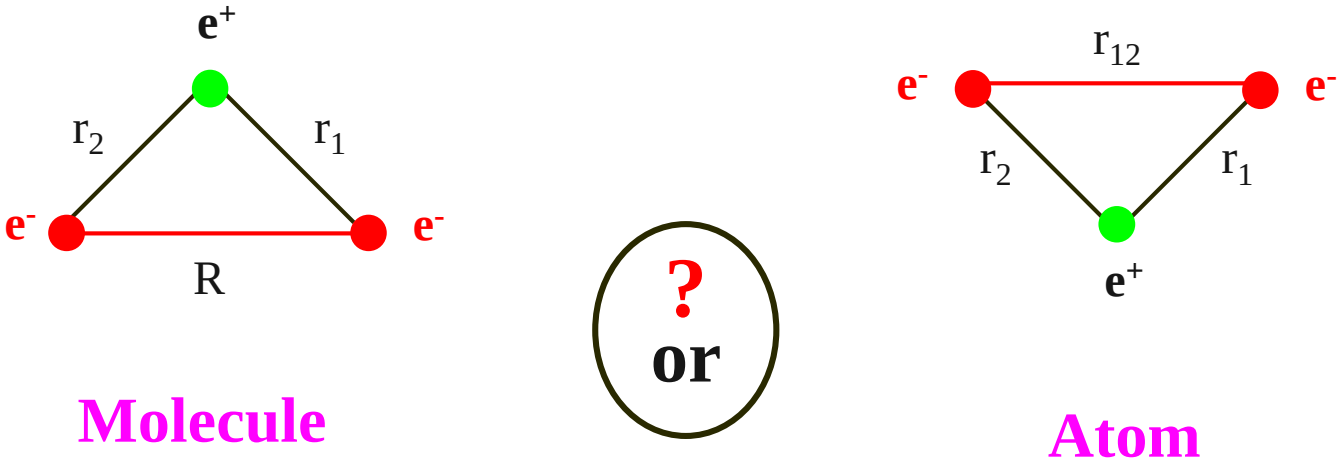
J. M. Rost[1] and D. Wintgen[2]

[1]*Department of Chemistry, University of Washington, BG-10, Seattle, Washington 98195*

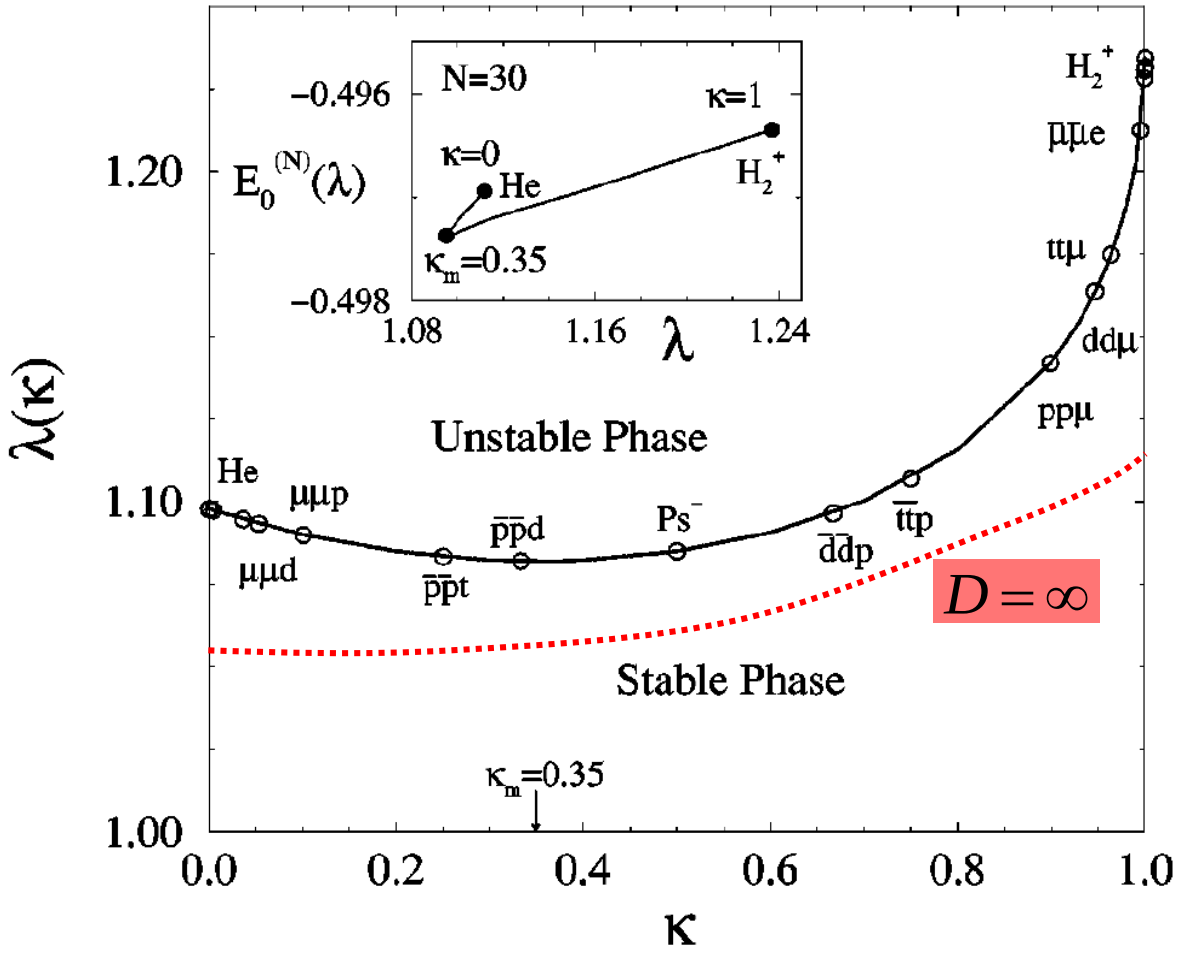
[2]*Fakultät für Physik der Universität, Hermann-Herder-Strasse 3 7800 Freiburg, Germany*

(Received 22 May 1992)

A highly accurate calculation is supplemented by an adiabatic approximation to explore the resonance spectrum of the positronium negative ion (Ps^-). Surprisingly, the spectrum can be understood and classified with H_2^+ quantum numbers by treating the interelectronic axis of Ps^- as an adiabatic parameter. We report and interpret the existence of ^1S shape resonances, a phenomenon so far unknown in three-body Coulomb systems. The new results on Ps^- combined with previous results for H^- suggest the existence of a resonance spectrum and its similarity for all *ABA* Coulomb systems with charges $|Z_A/Z_B| = 1$ and masses $m_A/m_B \geq 1$.



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

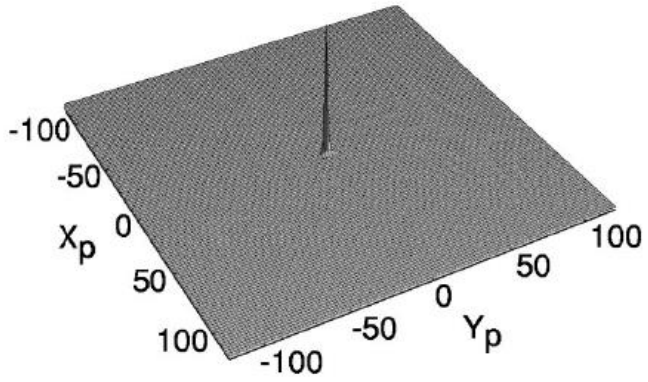
$(e^- \mu^+ e^-)$ Stable $(\mu^- p^+ \mu^-)$ Stable

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

Phase Transitions and Stability of Three Body Coulomb Systems

Charge density probability

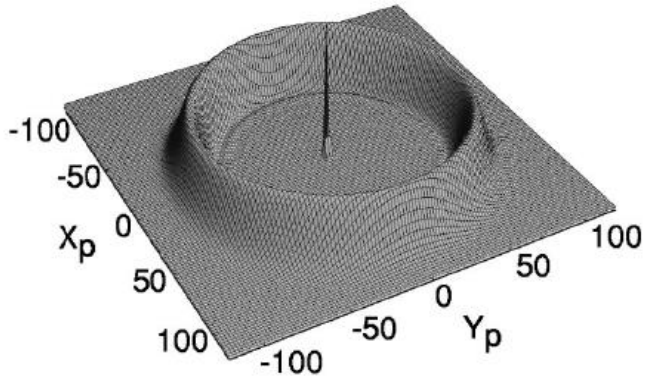
H_2^+



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

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

Bound States



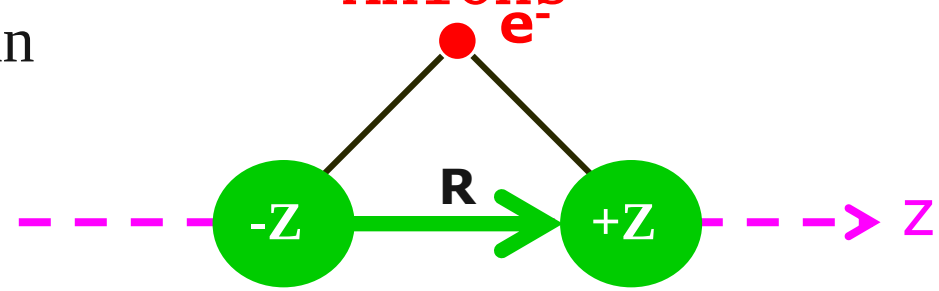
(b) $\lambda^{(N=20)} > \lambda_c^{(N=20)}$

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

Coulomb Explosion

FSS for Critical Conditions for Stable Dipole Bound Anions

The Hamiltonian



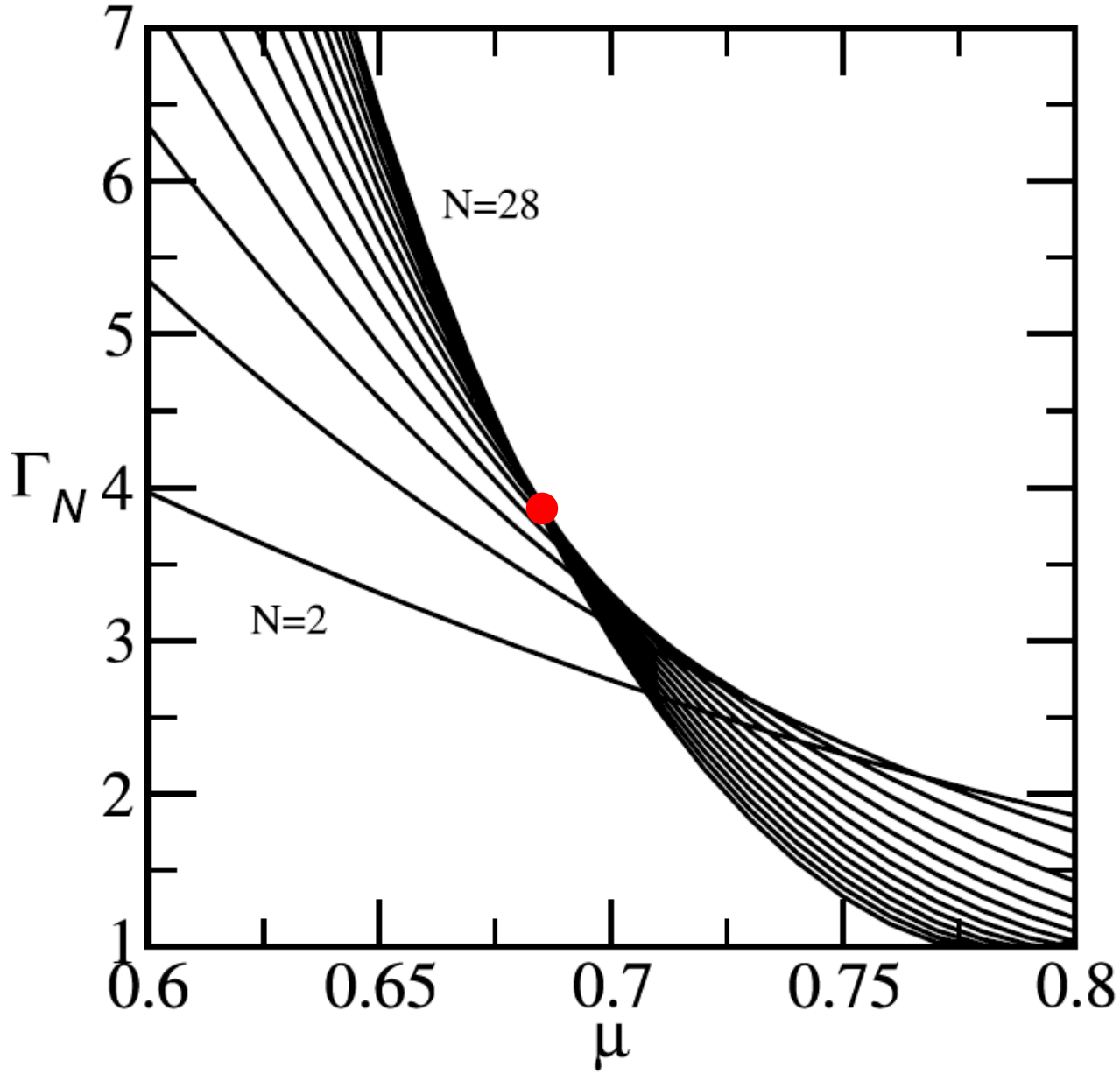
$$\mathscr{H}(Z;R;\vec{x}) = -\frac{1}{2}\nabla^2 - Z\left(\frac{1}{r} - \frac{1}{|\vec{r} - R\hat{k}|}\right)$$

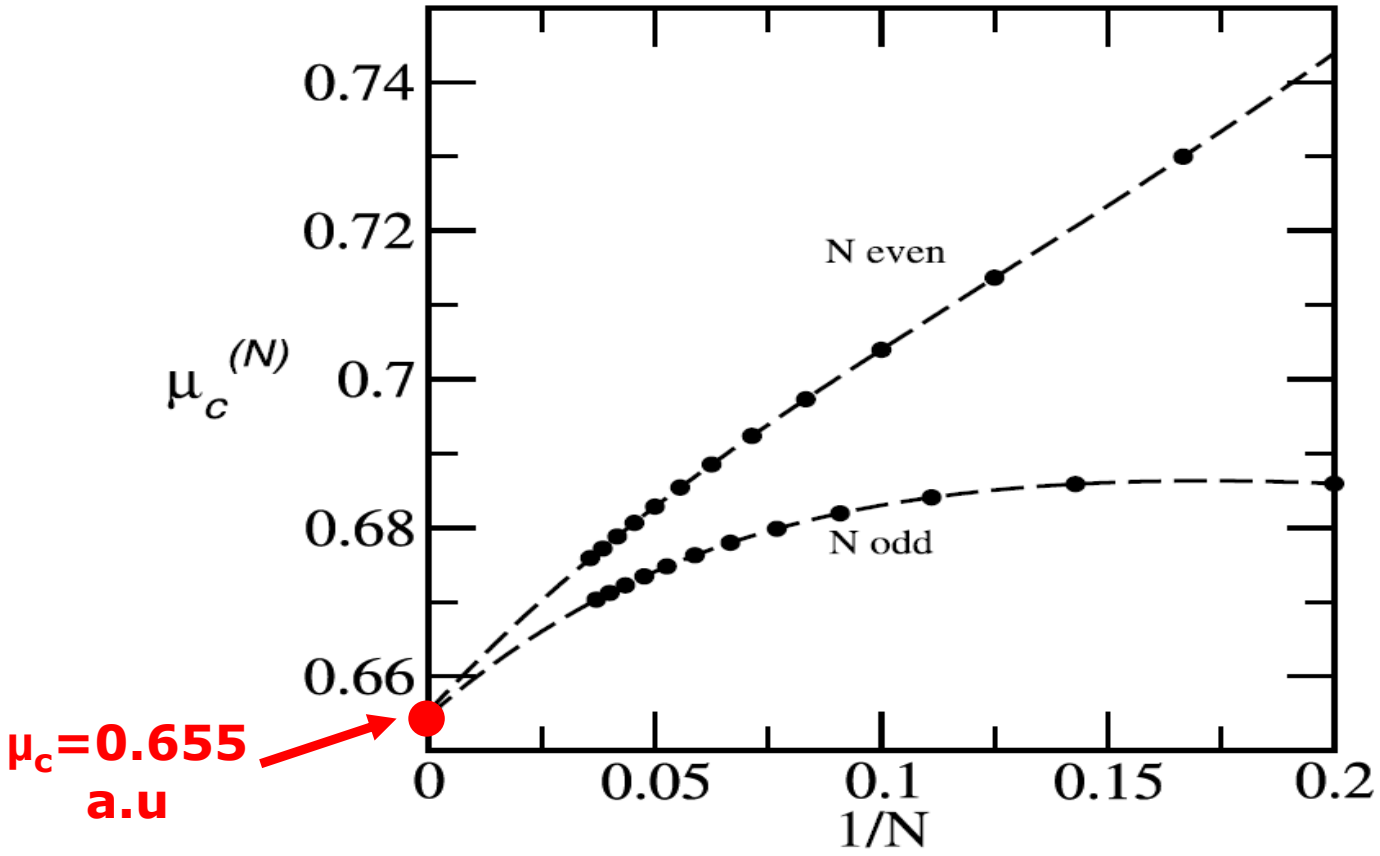
Slater Basis Set:

$$\Phi_{n,l}(\vec{r}) = \left[\frac{\alpha^{2n+3}}{(2n+2)!}\right]^{1/2} \mathrm{e}^{-\alpha r/2} r^n Y_l^0(\theta,\phi)$$

$$n = 0, 1, \ldots; \quad l = 0, \ldots, n,$$

Chem. Phys. Lett. 372,205 (2003)


7
6
5
4
3
2
1
Γ_N
N=28
N=2
0.6
0.65
0.7
0.75
0.8
μ



μ_c=0.655 a.u =1.625D without B.O =2.5D

Electron will be trapped with μ_c>2.5D

H_3C-CN	μ= 4.3 D	E_a=108 cm^-
H_2CCC	μ= 4.34 D	E_a=173 cm^-
$C_3H_4O_3$	μ= 5.5 D	E_a=40 meV
$C_3H_2O_3$	μ = 4.5 D	E_a=20 meV

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

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

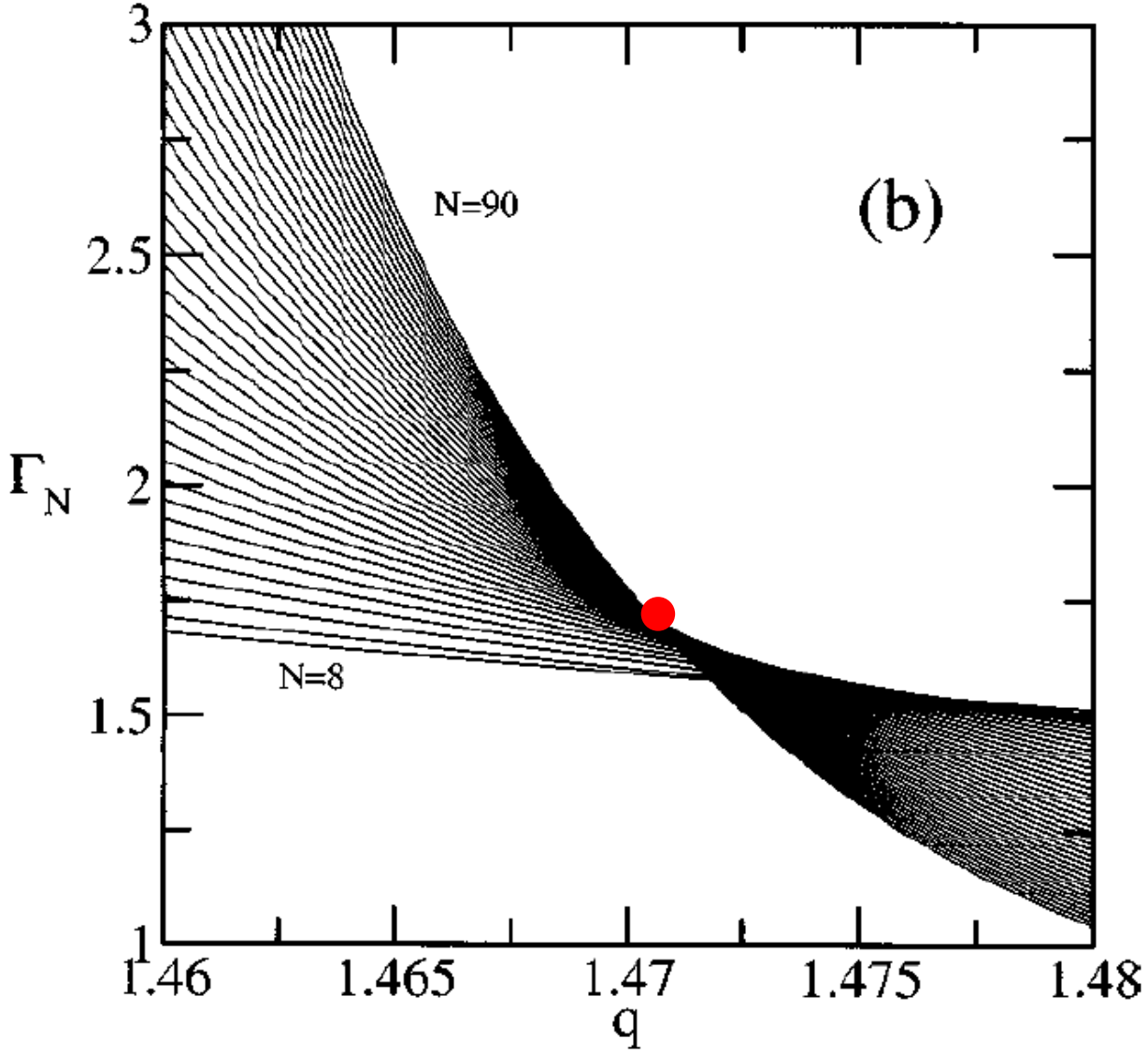
Slater Basis Set:

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

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

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

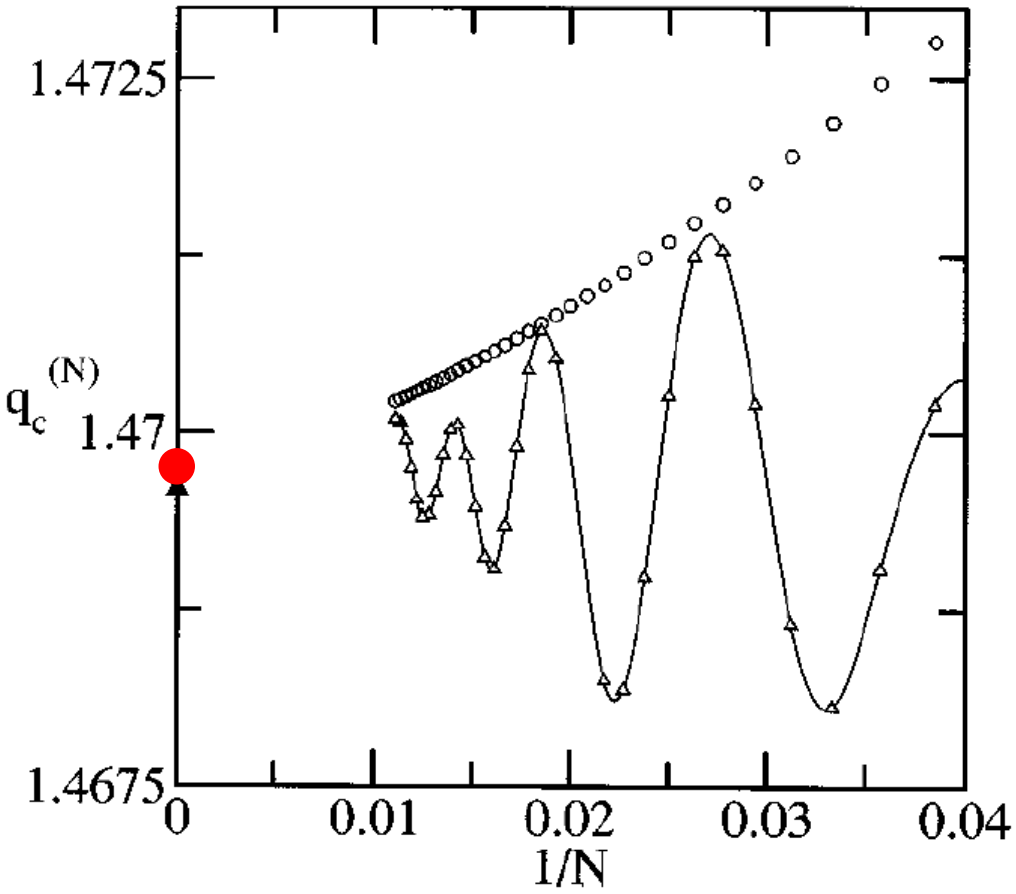
q ⟶ q=QR



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

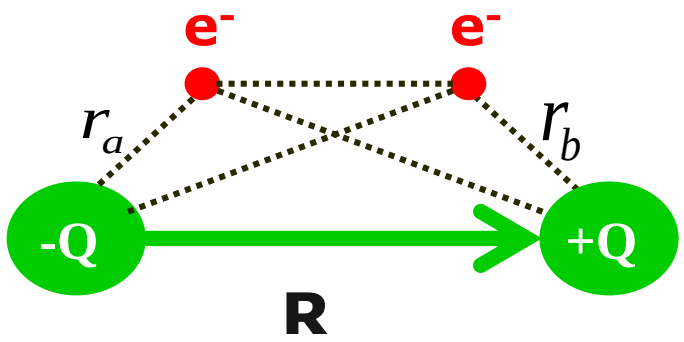
$(BeO)_2^-$ (13,13,0.5)

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

Journal of Chemical Physics, 120, 8412 (2004)

FSS for Critical Conditions for Stable Dipole-Bond Dianions

The Hamiltonian



$$\mathcal{H} = \sum_{i=1}^{2}\left[-\frac{1}{2}\nabla_i^2 - Q\left(\frac{1}{|\vec{r}_i - \vec{R}/2|} - \frac{1}{|\vec{r}_i + \vec{R}/2|}\right)\right] + \frac{1}{r_{12}},$$

Basis Set:

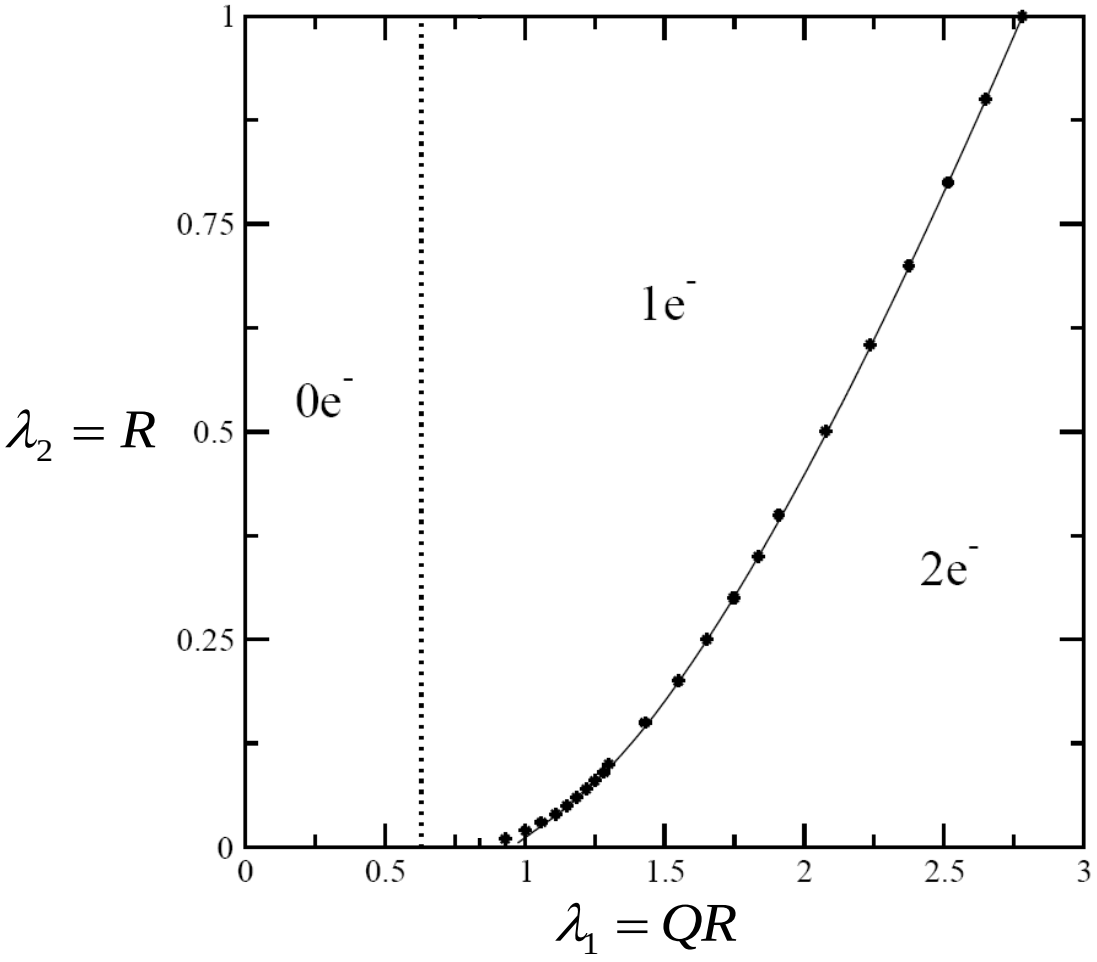
$$\Phi_n = Ce^{-\beta(\xi_1+\xi_2)}\left(\xi_1^{p_n}\eta_1^{q_n}\xi_2^{r_n}\eta_2^{s_n} + \xi_1^{r_n}\eta_1^{s_n}\xi_2^{p_n}\eta_2^{q_n}\right)r_{12}^{m_n},$$

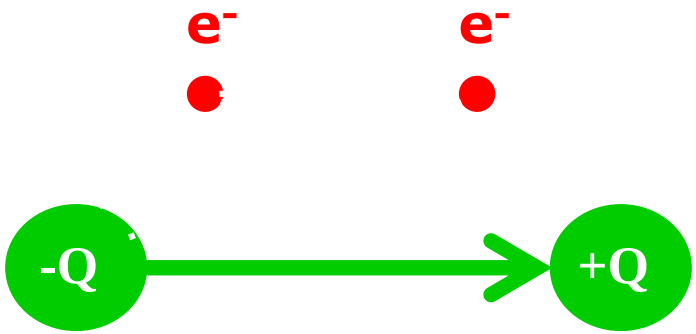
$$\xi = (r_a + r_b),\ \eta = (r_a - r_b),$$

Prolate spheroidal coordinates

J. Chem. Phys. (in press, 2007)

Stability diagram for two electron dipole





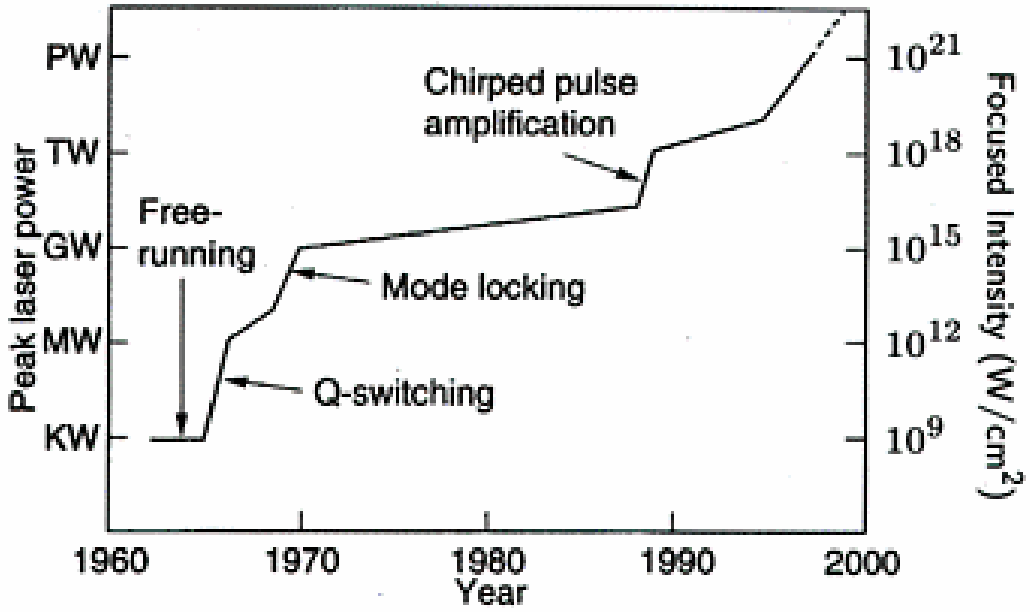
Atomic & Molecular Stabilization
by
Superintense Laser Fields

with

Prof. Dudley Herschbach
Harvard University

Multiply charged negative atomic ions in superintense laser fields

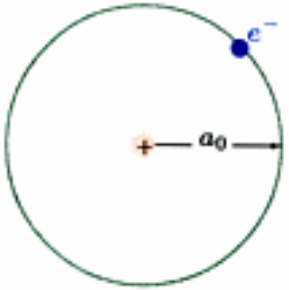
Superintense Laser Fields (I > a.u.)



"Strong Laser-Field": Intensities in the Range of $10^{13} \ldots 10^{16}$W/cm^2 Comparison: Electric field on 1st Bohr-Orbit in Hydrogen

$$E = \frac{1}{4\pi\epsilon_0}\frac{e}{a_0^2} = 5.1 \times 10^9 \text{V/m}$$

$$I = \frac{1}{2}\epsilon_0 c E^2 = 3.51 \times 10^{16} \text{W/cm}^2$$



At the same time: very short pulses possible:

≈ 5 fs (1 fs $= 10^{-15}$s)

$\approx 2 \ldots 4$ optical cycles in the visible region

The peak-power of pulsed lasers has increased by 12 orders of magnitude during the past 4 decades

QUESTION: What is the highest-level intensity presently possible?

ANSWER: The highest possible focused laser **intensity =10^{19} W/cm^2**

This level of intensity can be achieved with femtosecond laser based on Chirped Pulse Amplification (CPA).

Laser Atom Interaction

The electric field of a monochromatic plane wave can be written

$$E(t) = E_0(\hat{e}_x \cos\omega t + \tan\delta\, \hat{e}_y \sin\omega t)$$

With e_x and e_y orthogonal to each other and to the propagation direction

$\delta = 0$ corresponds to linear polarizati on

$\delta = \pm\pi/4$ corresponds to circular polarizati on.

$$\sum_{i=1}^{N}\left\{\frac{1}{2}p_i^{\,2} + \frac{1}{|\vec{r}_i + \vec{\alpha}(t)|} + \sum_{j=1}^{i-1}\frac{1}{|\vec{r}_i - \vec{r}_j|}\right\}\Psi = i\frac{\partial\Psi}{\partial t}$$

Moving frame of reference which follows the quiver motion of the classical electron

$$where\ \ \vec{\alpha}(t) = (\alpha_0/E_0)\vec{E}(t)$$

$\alpha_0 = E_0/\omega^2$, where E_0 and ω are the amplitude and frequency of the laser field.

High Frequency Floquet Theory

Hamiltonian of atomic system in super-intense laser fields

$$H = \text{kinetic term} + \text{coulomb term} + \text{laser term} + \text{e-e term}$$

$$H = \sum_{i=1}^{N} \left\{ \frac{1}{2} p_i^{\,2} + V_o(r_i, a_0) + \sum_{j=1}^{i-1} \frac{1}{|r_i - r_j|} \right\}$$

V_0 is the "dressed" Coulomb potential, is the time average of the shifted Coulomb over one period of the laser

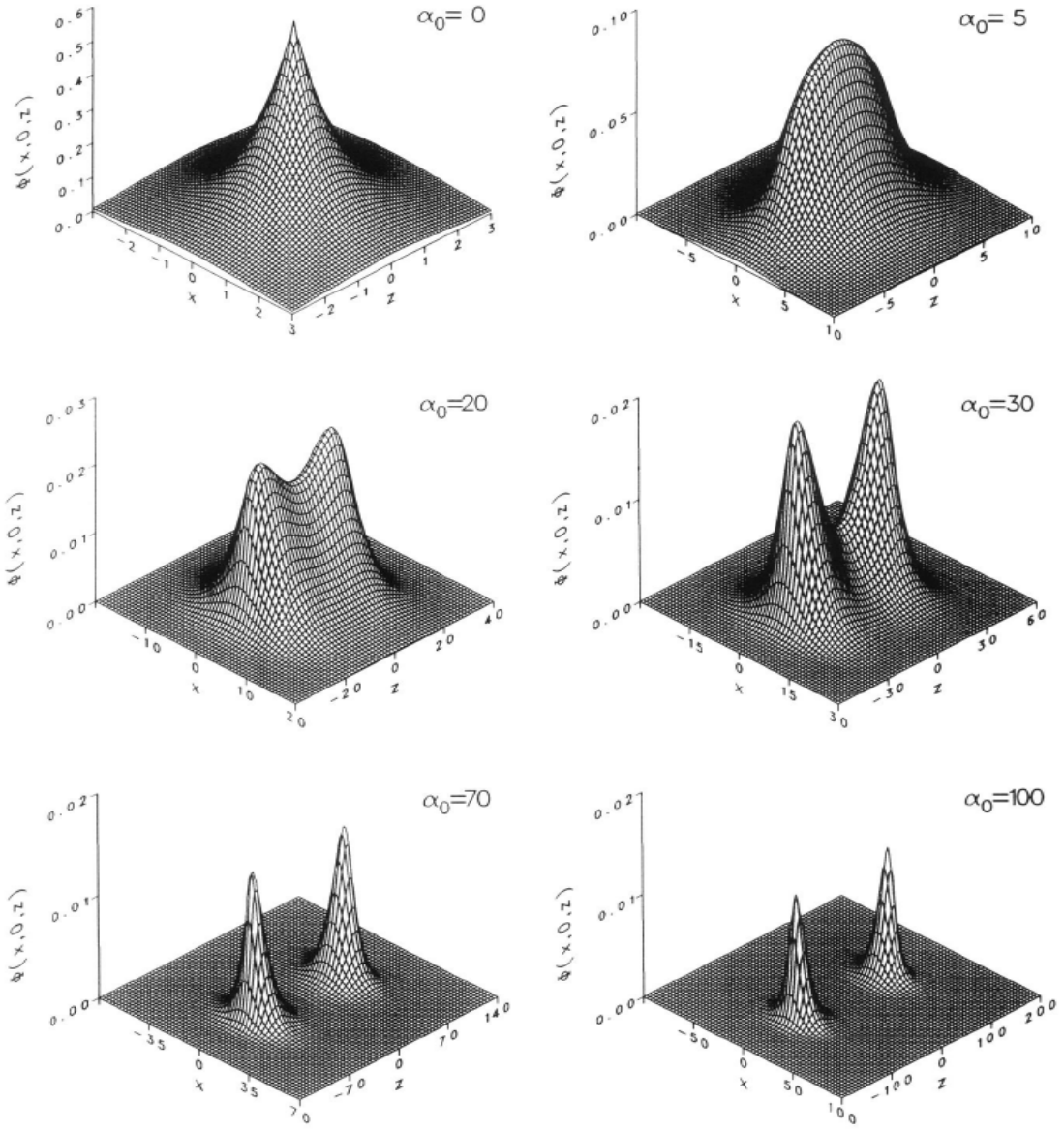
$$V_0(a_0, r) = -\frac{1}{2\pi} \int_0^{2\pi} \frac{d\phi}{\left| \vec{r} + a_0 (\hat{e}_x \cos\phi + \tan\delta\, \hat{e}_y \sin\phi) \right|}$$

$\alpha_o = \sqrt{I}/\omega^2$, where I is the time - averaged beam intensity and ω is the frequency.

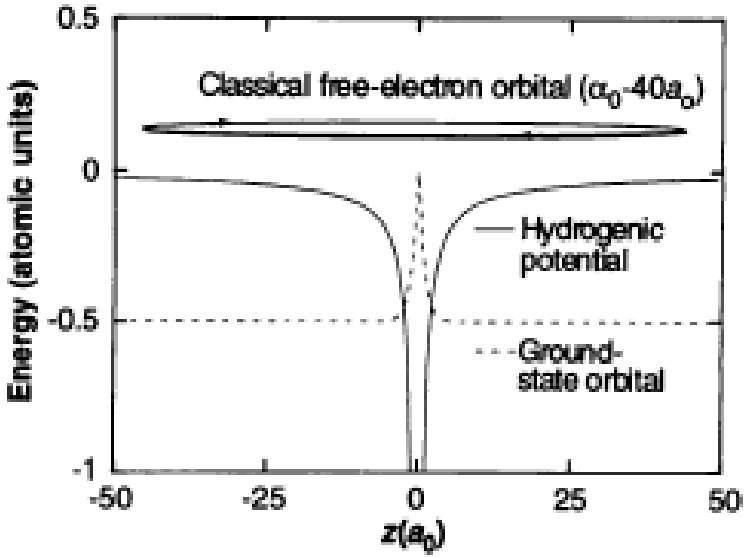
Structure Equation:

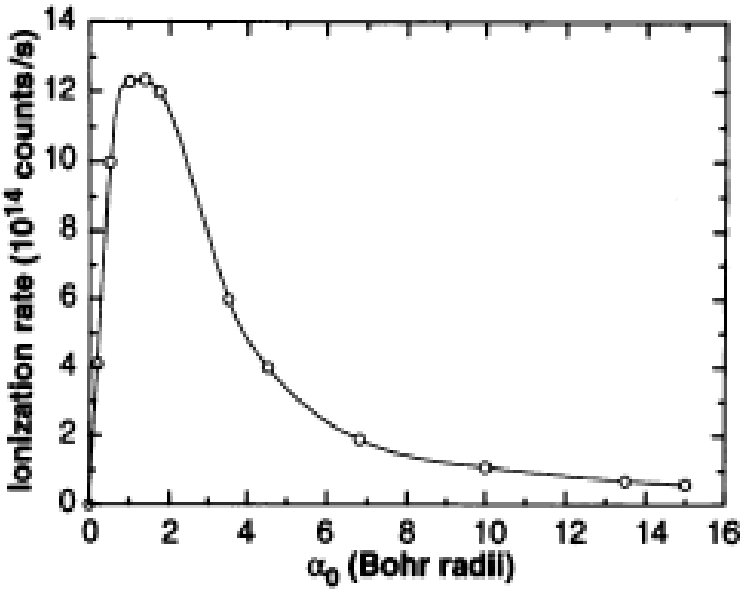
$$H\,\Psi = E(\alpha_0)\,\Psi$$

Hydrogen atom in super-intense linear laser fields



M. Pont, *et al*. Phys. Rev. Lett. 61, 939 (1988)

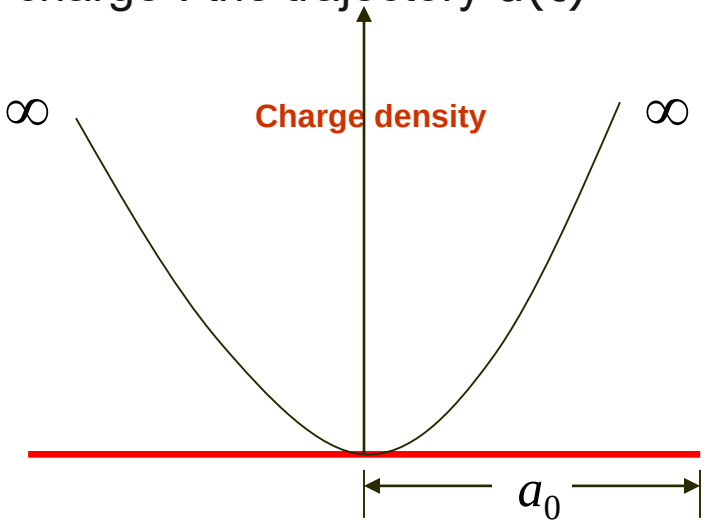




J. H. Eberly, *et al* Science 262, 1229 (1993)

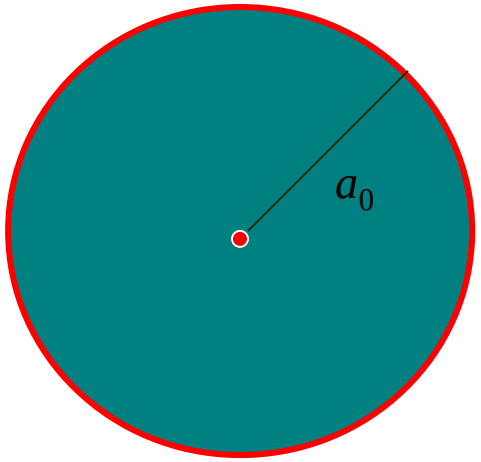
Linear Charge and Circular Charge

For linear polarization, the "dressed" potential is the same as that generated by a "linear charge": the trajectory $\alpha(t)$



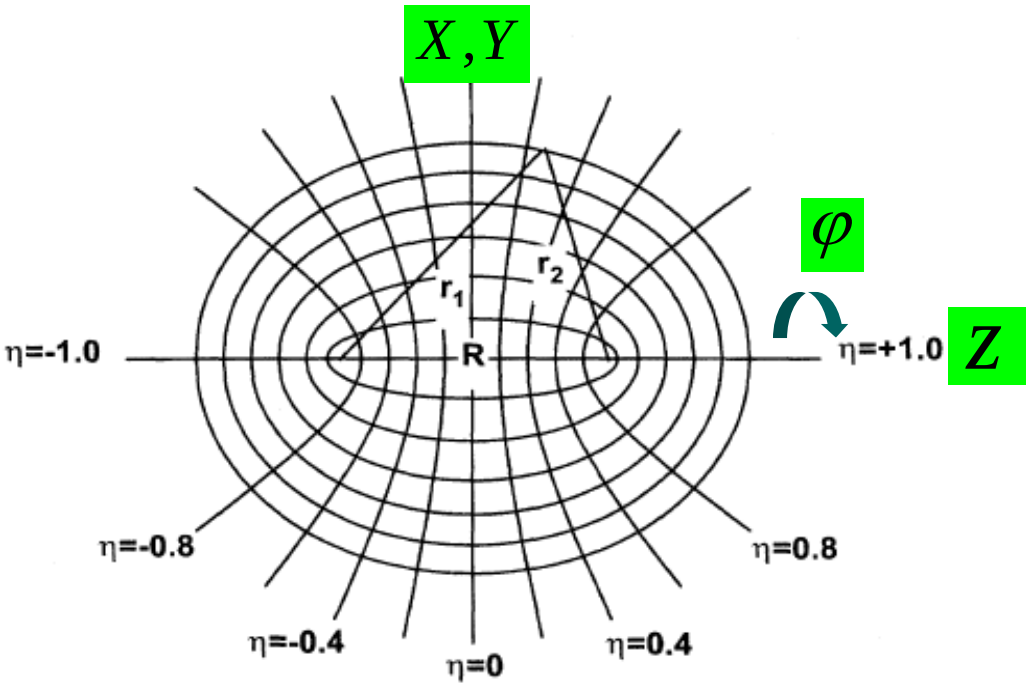
Linear charge

For circular polarization, the "dressed" potential is the same as that generated by a "circular charge".



Circular charge

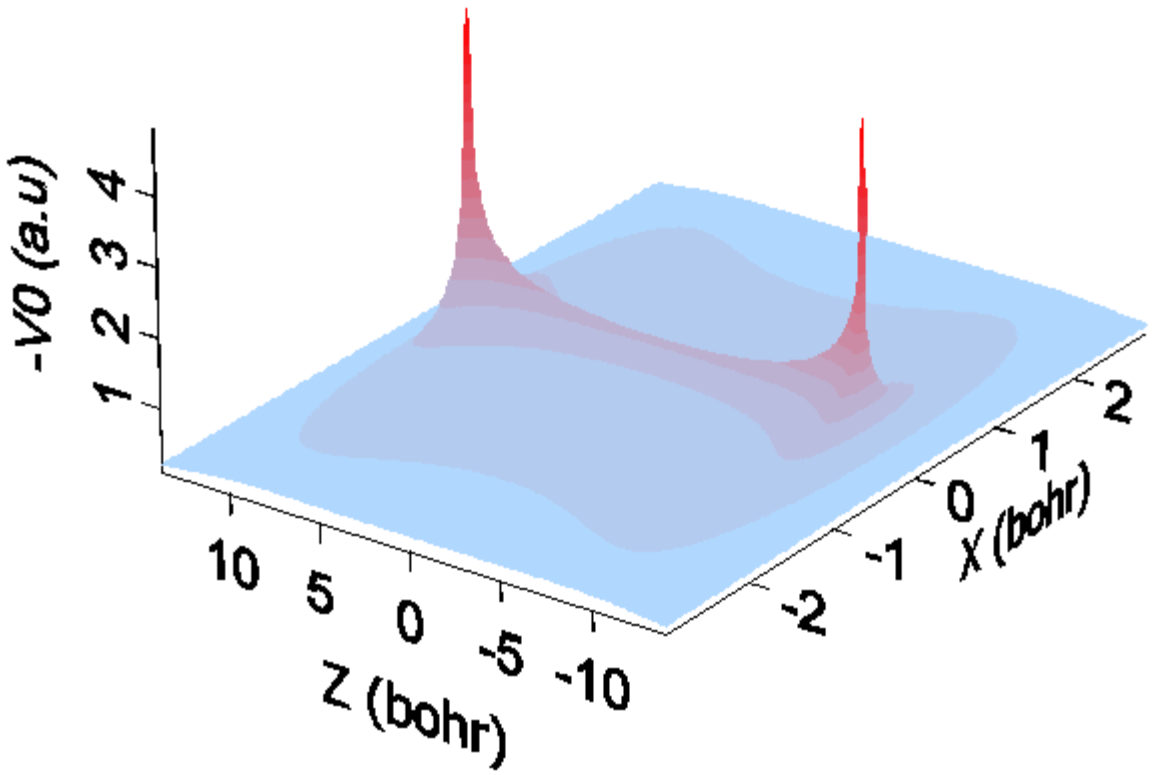
Prolate Spheroidal Coordinates for Linear Polarization



$$\xi = \frac{r_1 + r_2}{R}, \qquad 1 \leqslant \xi \leqslant \infty$$

$$\eta = \frac{r_1 - r_2}{R}, \qquad -1 \leqslant \eta \leqslant 1$$

$$0 \leqslant \varphi \leqslant 2\pi.$$


-V0 (a.u)
1
2
3
4
10
5
0
-5
-10
Z (bohr)
-2
-1
0
1
2
X (bohr)

Basis Set (Linear Polarization)

One-electron basis functions in elliptical coordinates

$$\psi(\xi,\eta,\phi)_{p,q,m} = (\xi-1)^p \eta^q \left[(1-\eta^2)(\xi^2-1)\right]^{m/2} e^{im\phi} e^{-\gamma\xi}$$

p, q and m are non - negative integers.

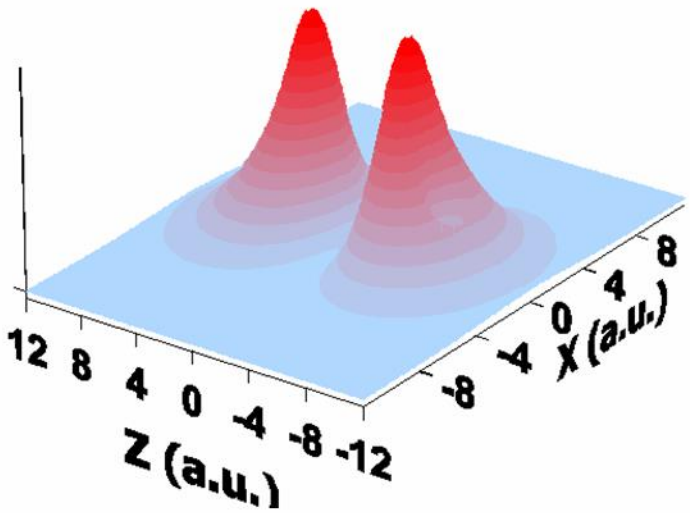
γ is a parameter to optimize the energy

For ground state, $m = 0$, so the basis becomes :

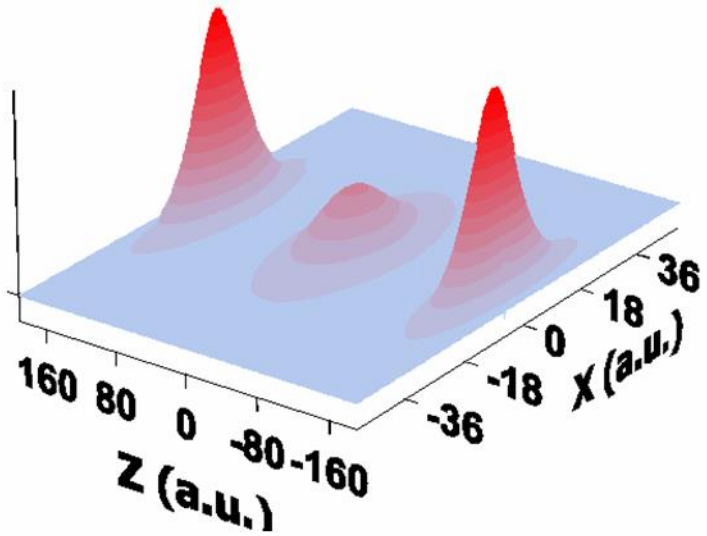
$$\psi(\xi,\eta,\phi)_{p,q,m} = (\xi-1)^p \eta^q e^{-\gamma(\xi-1)}$$

We used about 100 basis functions

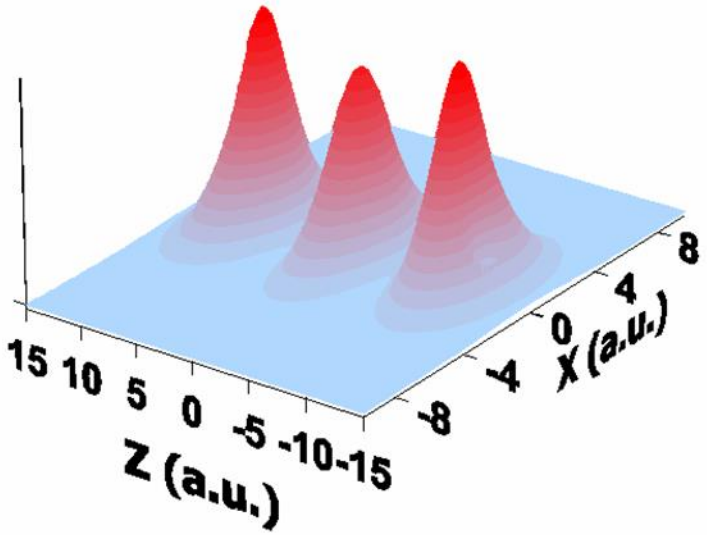
H^-


12 8 4 0 -4 -8 -12
Z (a.u.)
-8 -4 0 4 8
X (a.u.)

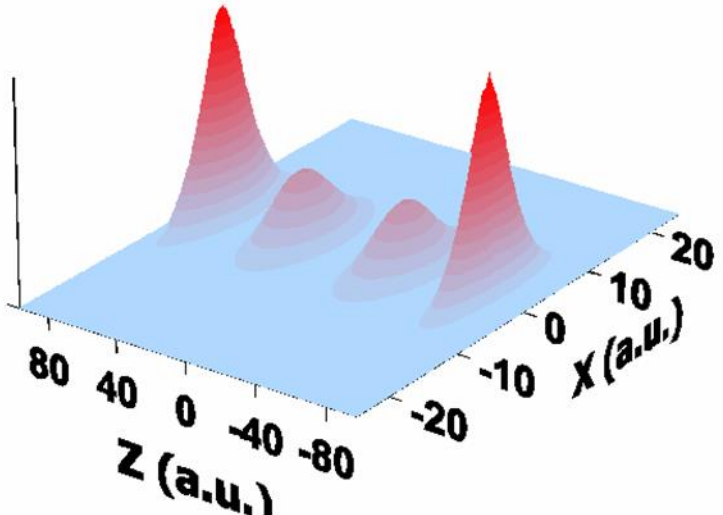
H^{2-}

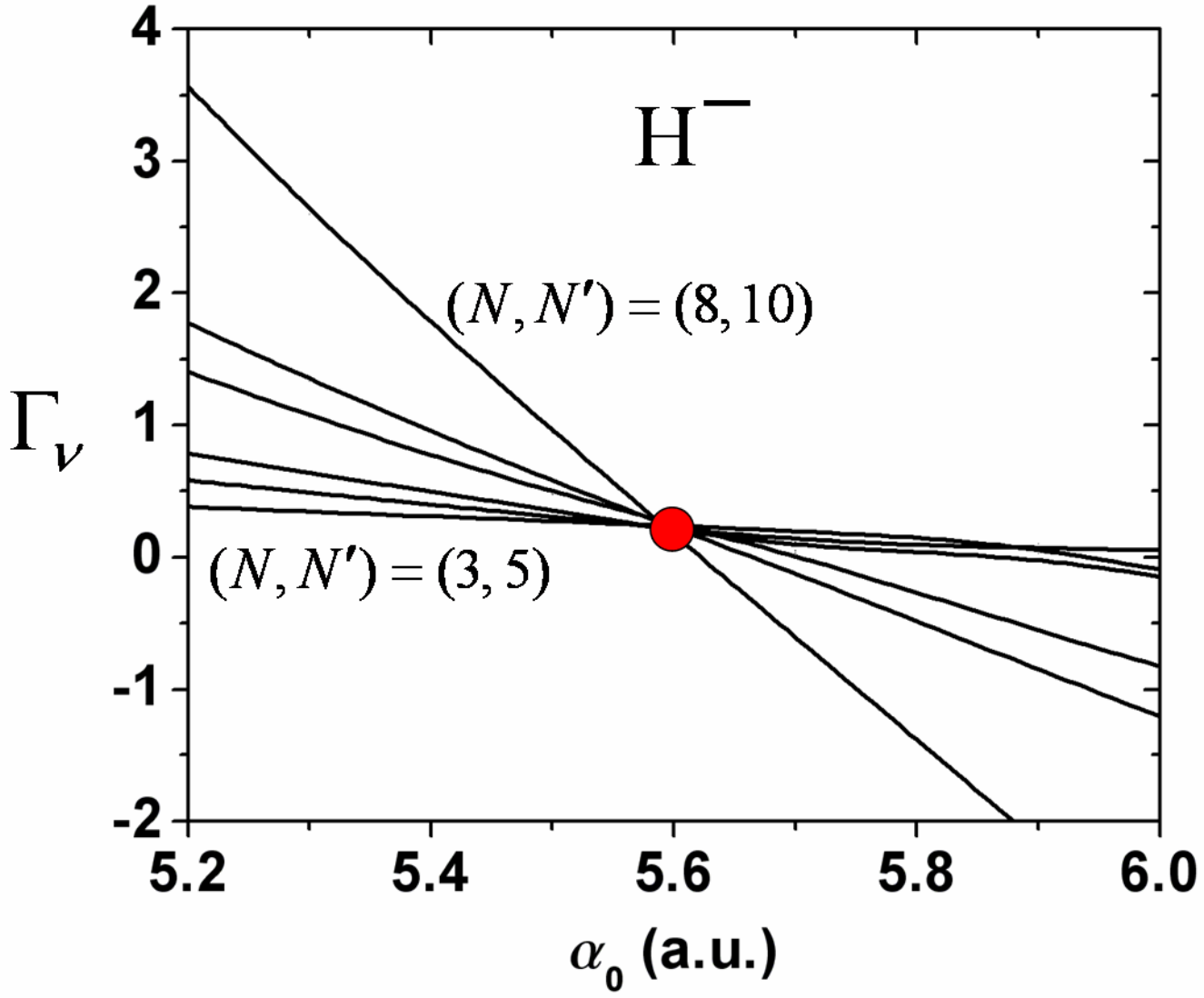

160 80 0 -80 -160
Z (a.u.)
-36 -18 0 18 36
X (a.u.)

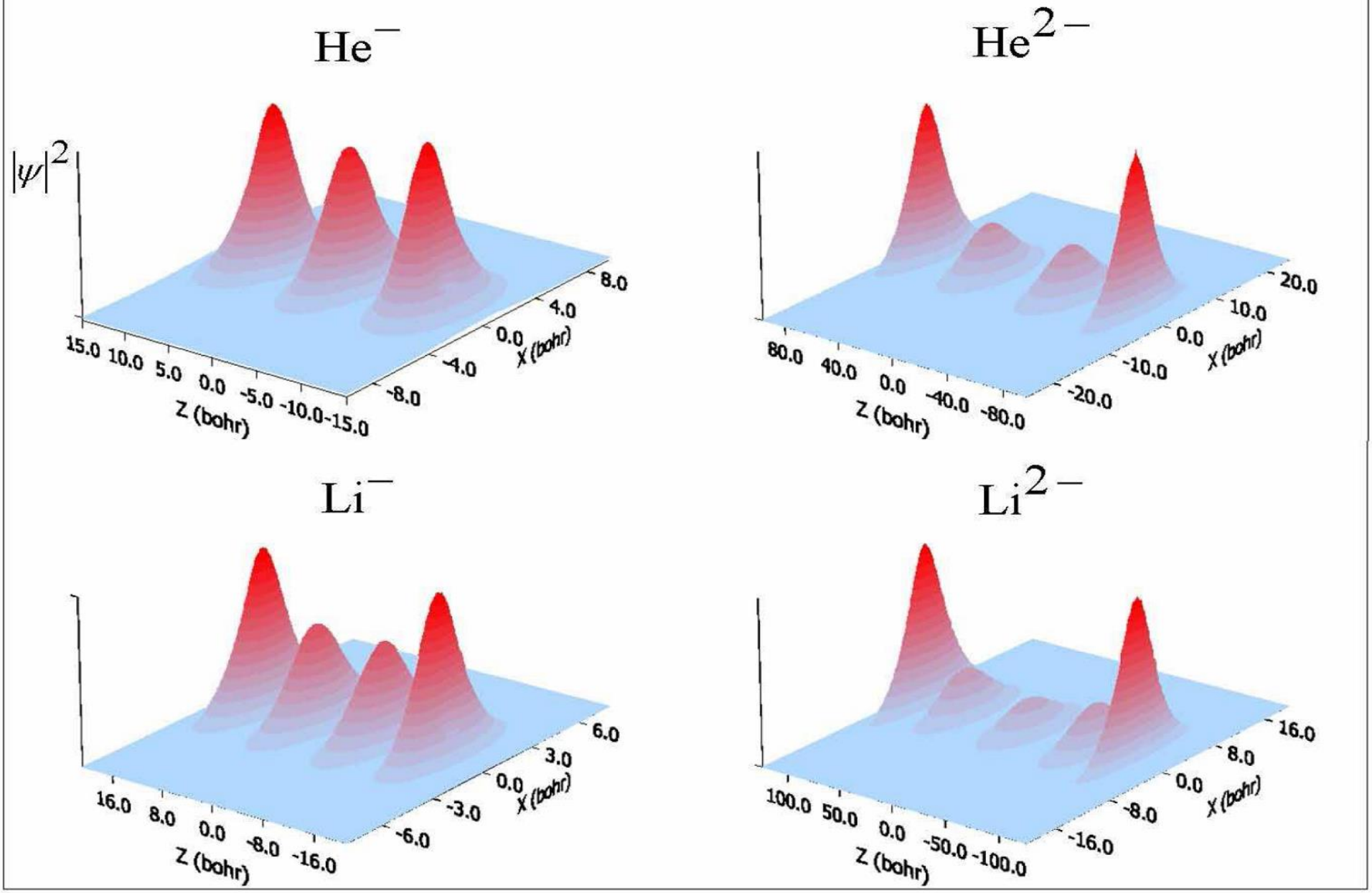
He^-


15 10 5 0 -5 -10 -15
Z (a.u.)
-8 -4 0 4 8
X (a.u.)

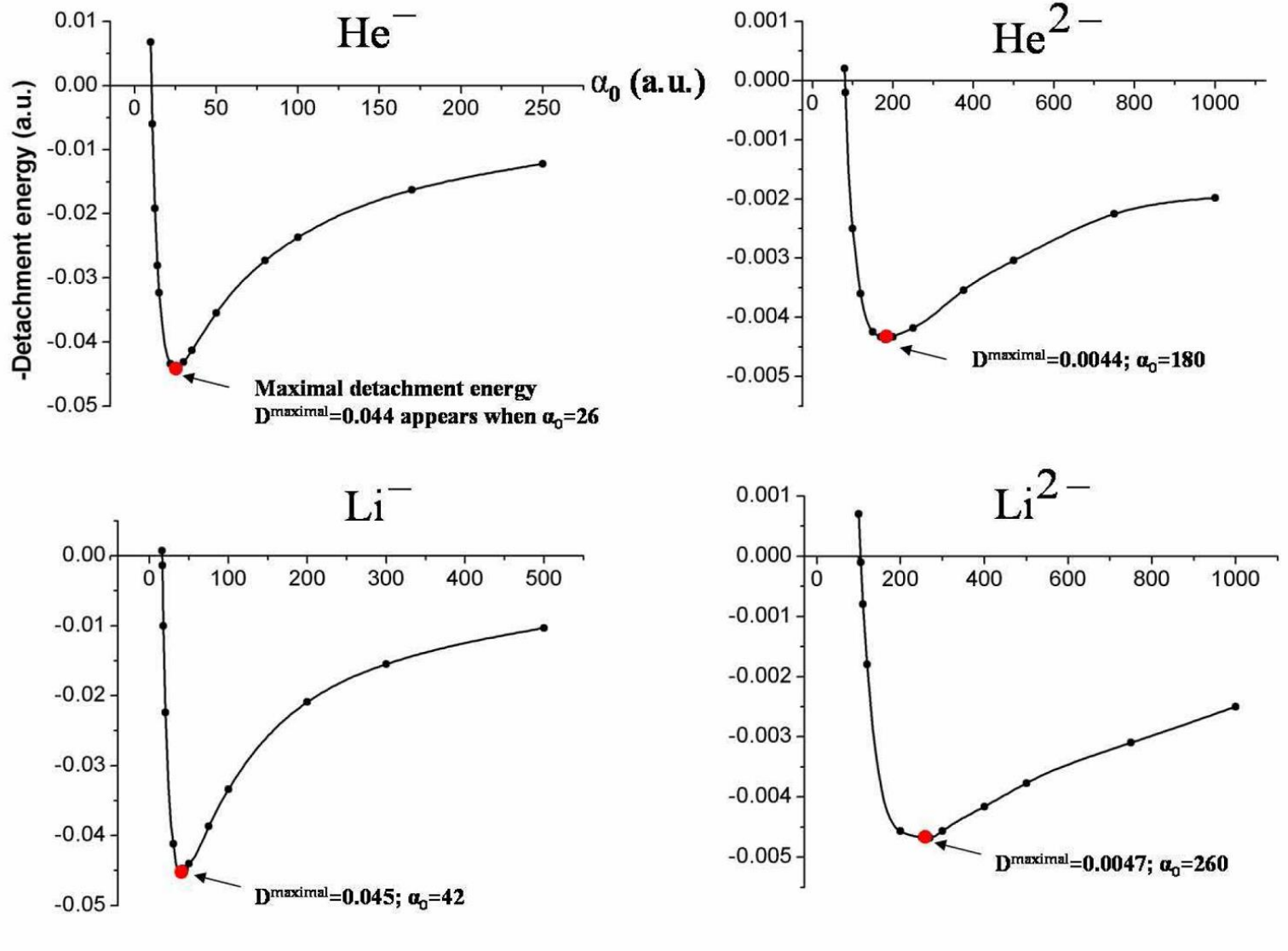
He^{2-}


80 40 0 -40 -80
Z (a.u.)
-20 -10 0 10 20
X (a.u.)


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



The electronic orbitals for the ground states. The presentation is given in a plane passing through the axis of the field taken as polar axis z



Negative of the detachment energy of the ground state of He^-, He^{2-}, Li^-,and Li^{2-} in a linearly polarized high-frequency laser field as a function of $\alpha_0=E_0/\omega^2$, where E_0 and ω are the amplitude and frequency of the laser field.

Critical parameters for stability of He^-, He^{2-}, Li^- and Li^{2-} in superintense laser fields. The intensity is determined by the following equation: $I(W/cm^2) = |E_0(a.u.)|^2 \times 3.509 \times 10^{16}$, where $E_0 = \omega^2 \alpha_0$, we choose $\omega = 5eV$

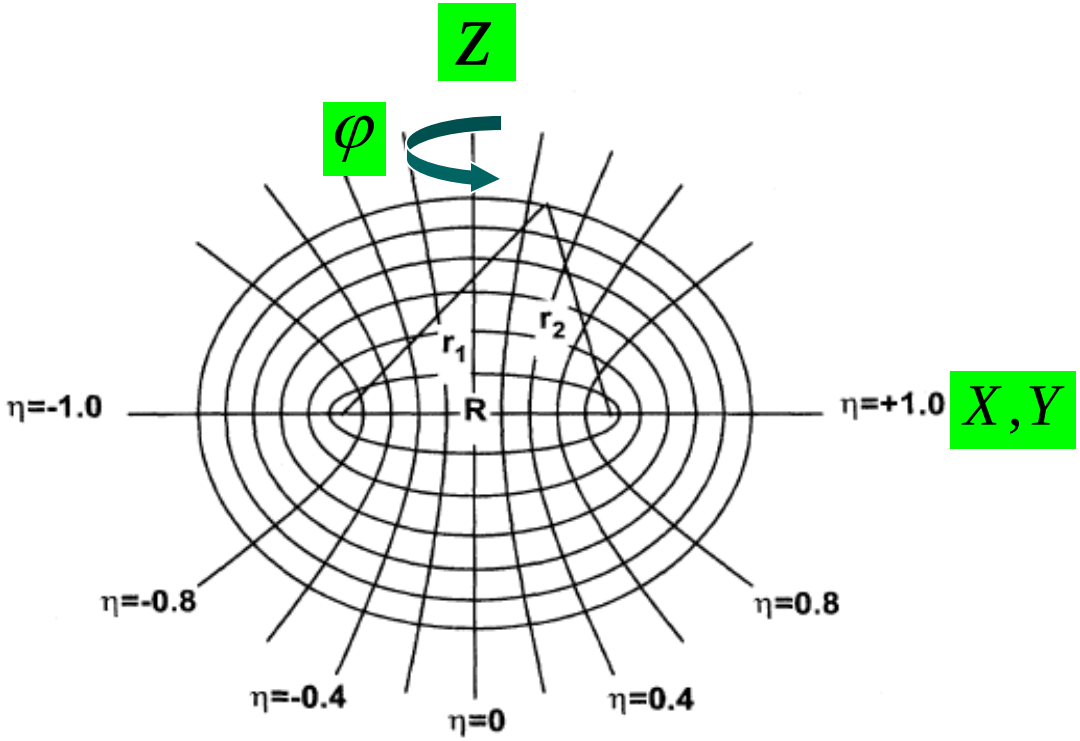
For example, when ultra-high-power KrF laser (5 eV photons) are used, the peak intensity in the experiments should be I ≈ 10^{16}W/cm^2

	$\alpha_0^{critical}(a.u.)$	$I^{critical}(W/cm^2)$	$\alpha_0^{maximum}(a.u.)$	$I^{maximum}(W/cm^2)$	Detachment Energy (eV)
He^-	11	4.8×10^{15}	26	2.7×10^{16}	1.2
He^{2-}	82	2.7×10^{17}	180	1.3×10^{18}	0.12
Li^-	16	1.0×10^{16}	42	7.1×10^{16}	1.2
Li^{2-}	105	4.4×10^{17}	250	2.5×10^{18}	0.13

$$Detachment\ energy = E^{N-1} - E^N \geq 0$$

The energy needed to detach one of the N electrons

Oblate Spheroidal Coordinates for Circular Polarization



$$\xi = \frac{r_1 + r_2}{R}, \qquad 1 \leqslant \xi \leqslant \infty$$

$$\eta = \frac{r_1 - r_2}{R}, \qquad -1 \leqslant \eta \leqslant 1$$

$$0 \leqslant \varphi \leqslant 2\pi.$$

Basis Set (Circular Polarization)

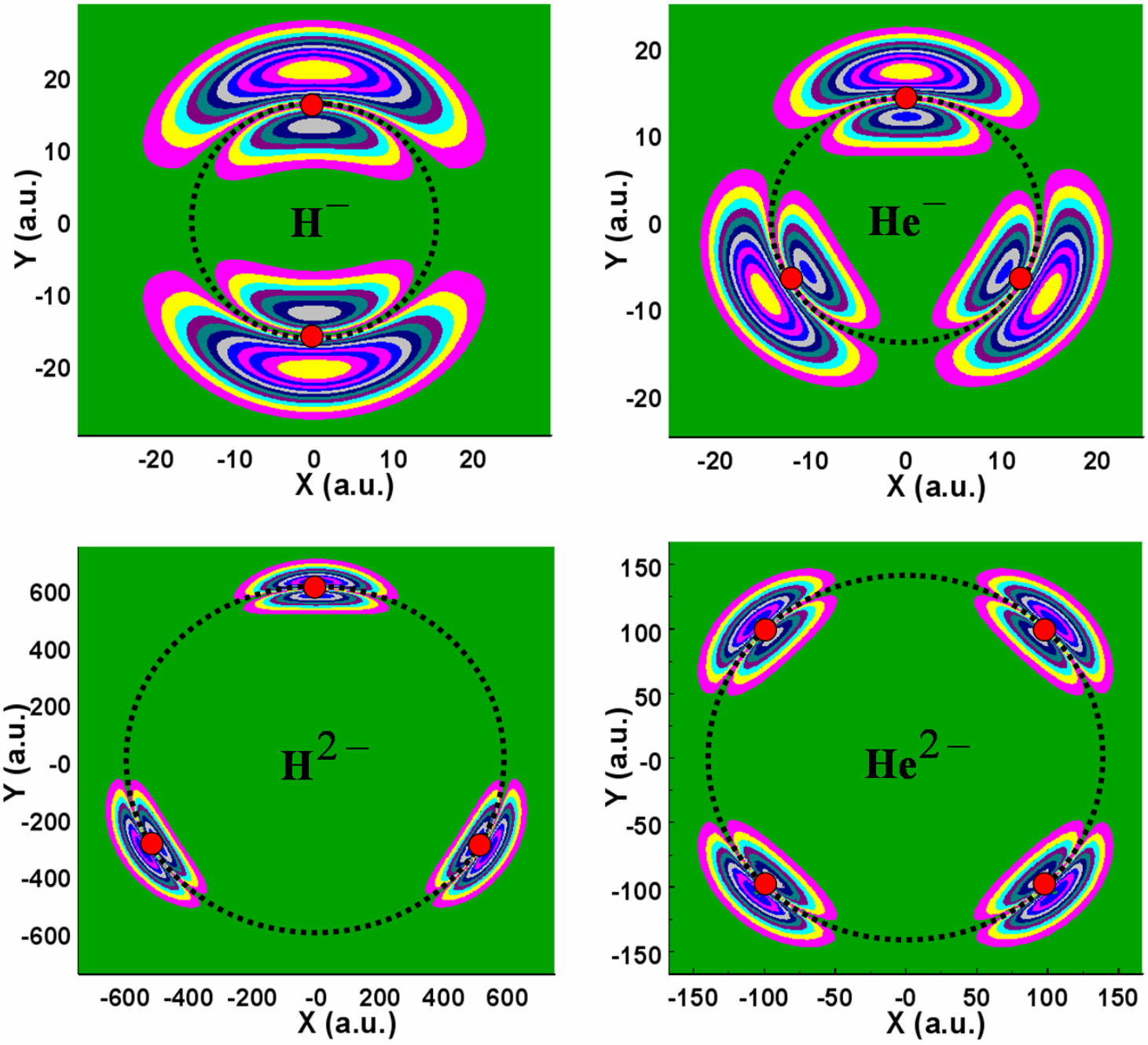
$$\psi_{p,q,m}(\xi,\eta,\varphi) = (\xi-1)^p \eta^q e^{-\gamma\xi} S_m(\varphi)$$

$$\psi_{p,q,m}(\xi,\eta,\varphi) = (\xi-1)^p \eta^q e^{-\gamma\xi} \cdot \begin{cases} \frac{1}{\sqrt{\pi}}\cos(m\varphi) & \mathbf{m > 0} \\ \frac{1}{\sqrt{2\pi}} & \mathbf{m = 0} \\ \frac{1}{\sqrt{\pi}}\sin(|m|\varphi) & \mathbf{m < 0} \end{cases}$$

$p = n - l - 1;\ q = l - m;\ m = -l, -l+1, \ldots l$

γ is a parameter to optimize the energy

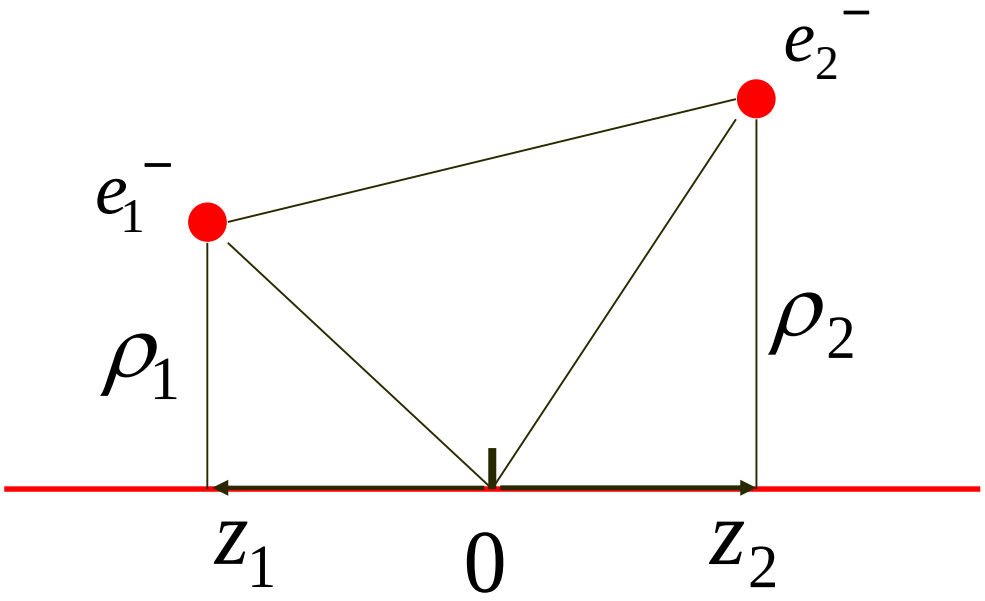
We used over 200 basis functions


H⁻
He⁻
H²⁻
He²⁻
X (a.u.)
Y (a.u.)

Large-D stability in Linearly polarized superintense laser fields

$$H = \frac{1}{2}\sum_{i=1}^{N}\frac{1}{\rho_i^{\,2}} + \sum_{i=1}^{N} V_0(\rho_i, z_i) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\sqrt{\rho_i^{\,2} + \rho_j^{\,2} + (z_i - z_j)^2}}$$

$$V_0(\rho_i, z_i) = \frac{-Z}{2\pi}\int_0^{2\pi}\frac{d\phi}{\sqrt{\rho_i^{\,2} + (z_i + \alpha_0 Sin\phi)^2}}$$

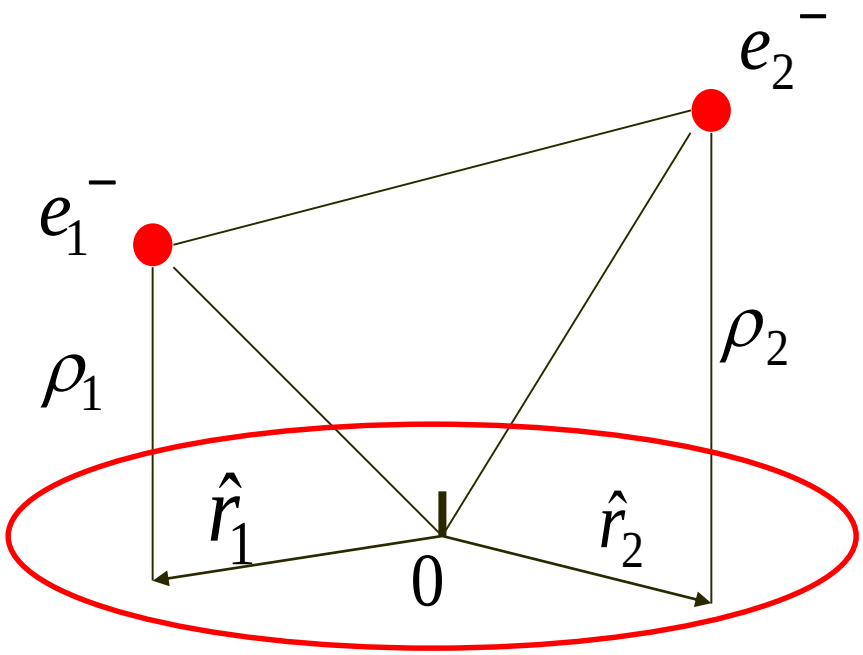


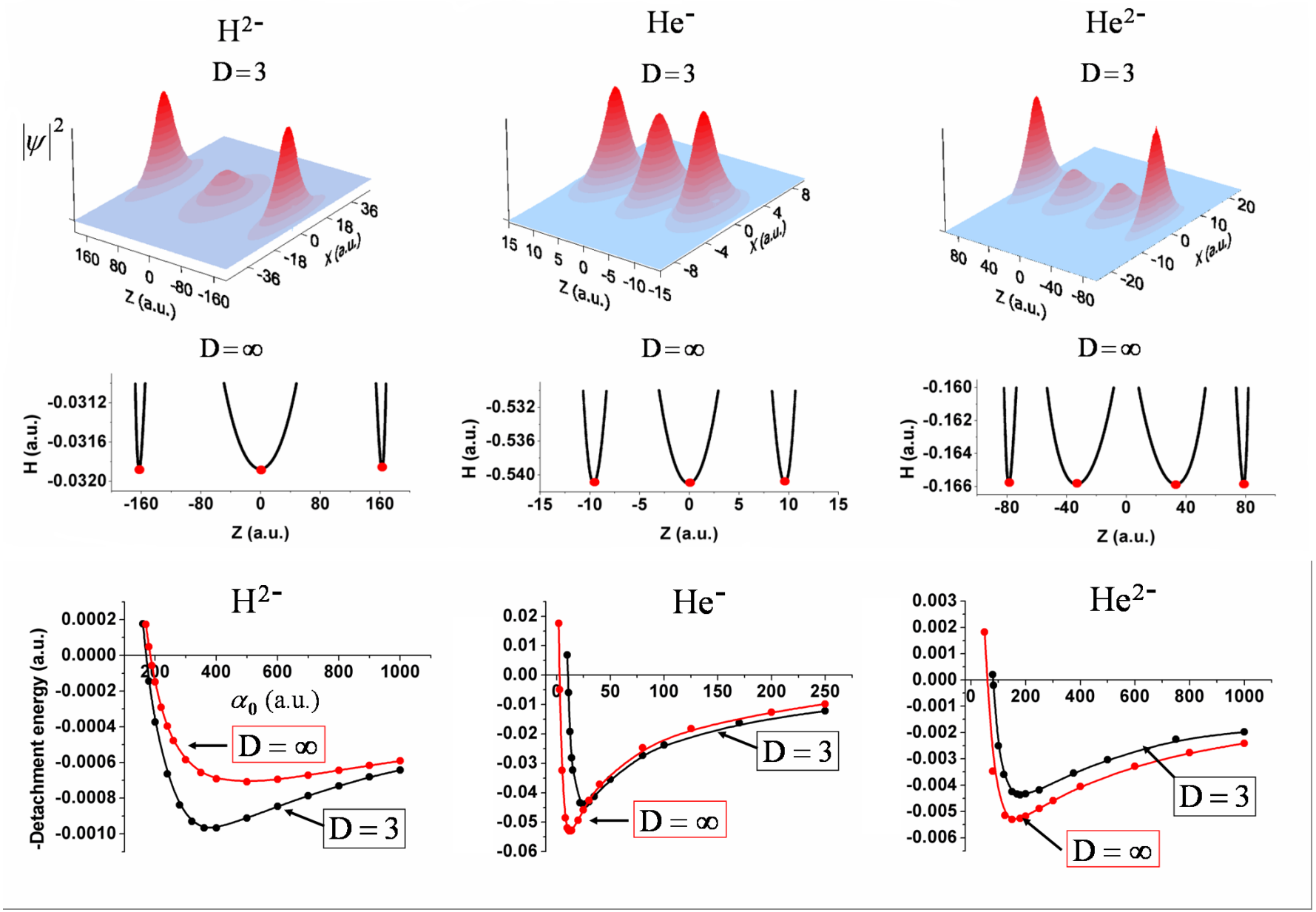
Dudley Herschbach, Harvard

Large D stability in super-intense circular polarized laser fields

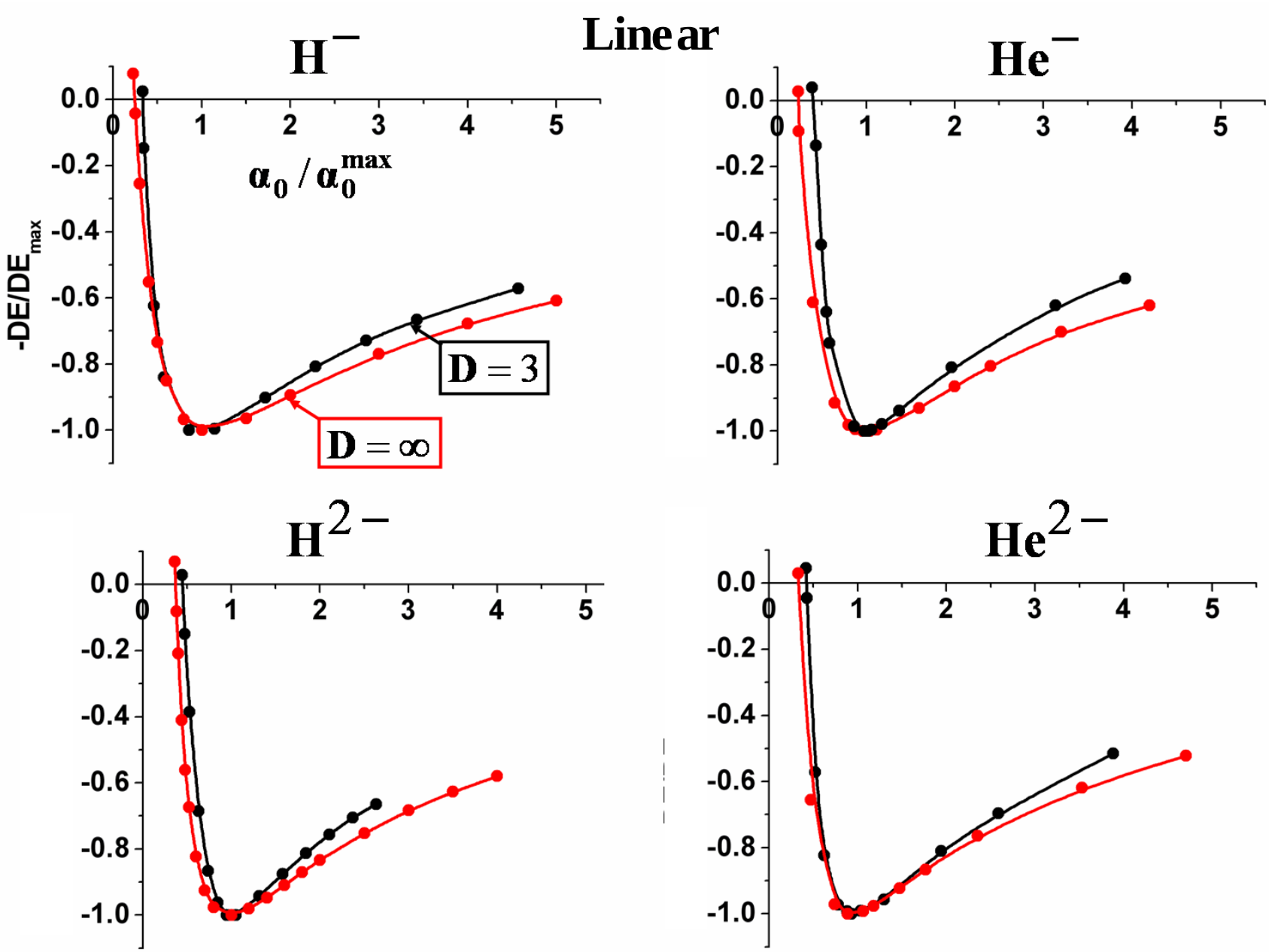
$$\mathrm{H} = \frac{1}{2}\sum_{i=1}^{N}\frac{1}{{\rho_i}^2} + \sum_{i=1}^{N} V_0(\rho_i, \hat{r}_i) + \sum_{i=1}^{N}\sum_{j=i+1}^{N}\frac{1}{\sqrt{{\rho_i}^2 + {\rho_j}^2 + (\hat{r}_i - \hat{r}_j)^2}}$$

$$V_0(\rho_i, \hat{r}_i) = \frac{-Z}{2\pi}\int_0^{2\pi}\frac{d\phi}{\sqrt{{\rho_i}^2 + (\hat{r}_i \cdot \hat{e}_x + \alpha_0 Cos\phi)^2 + (\hat{r}_i \cdot \hat{e}_y + \alpha_0 Sin\phi)^2}}$$

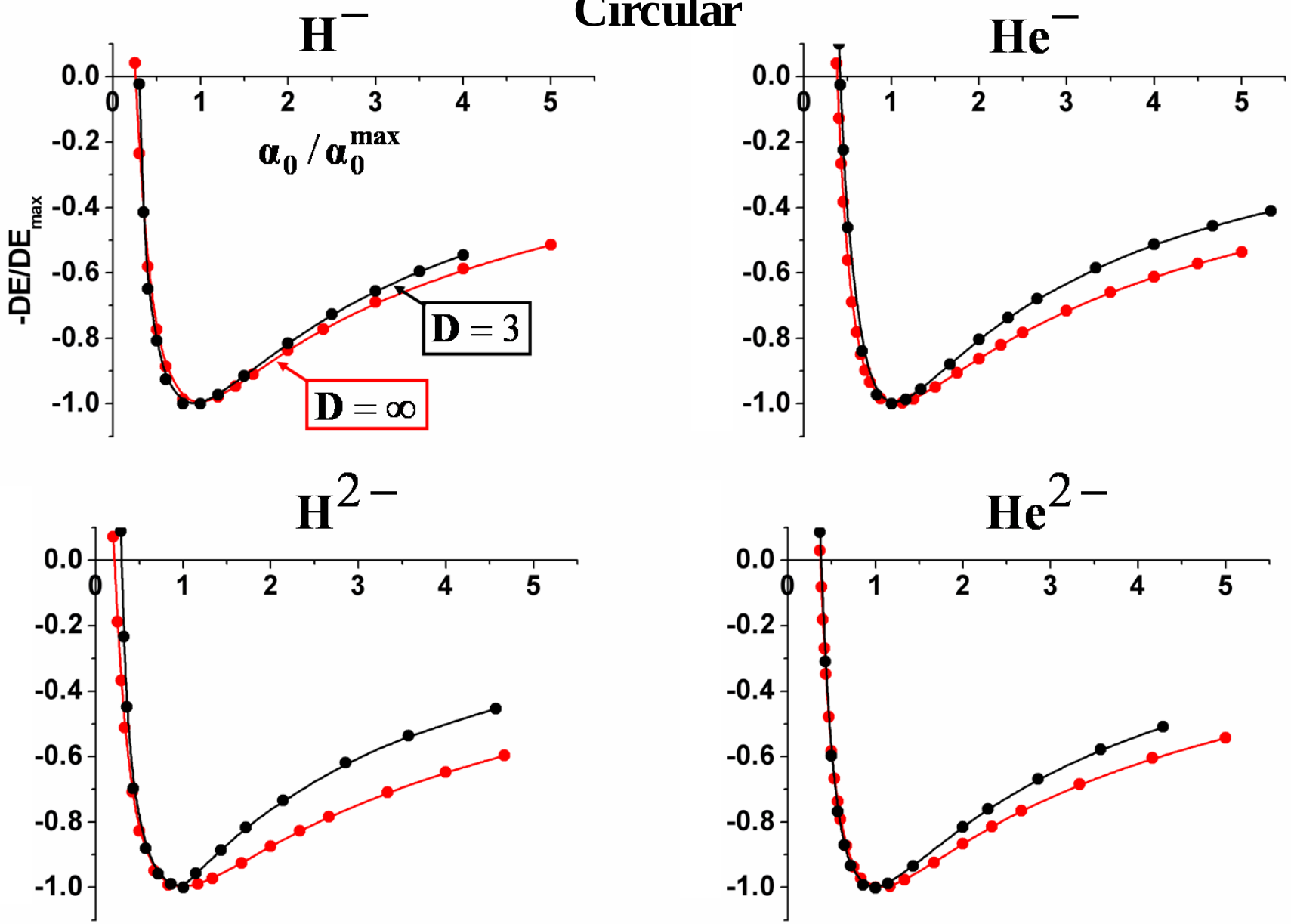




Negative of the detachment energy of the ground state of He^-,H^{2-} and He^{2-} in a circularly polarized high-frequency laser field as a function of $\alpha_0=E_0/\omega^2$, where E_0 and ω are the amplitude and frequency of the laser field.


Linear
H⁻
He⁻
H²⁻
He²⁻
-DE/DE_max
α₀ / α₀^max
D = 3
D = ∞
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0
1
2
3
4
5

Circular

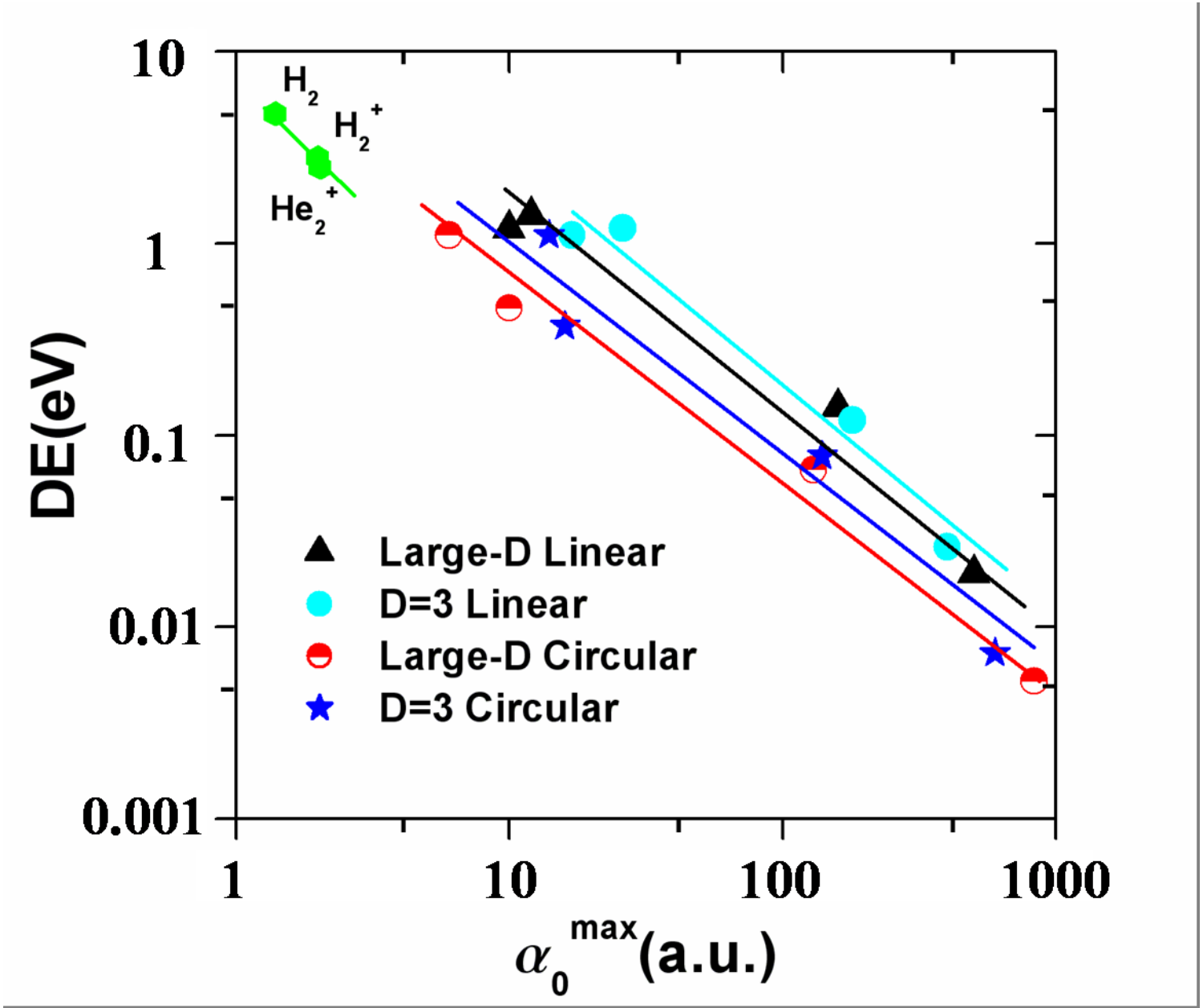


Critical parameters for stability of atomic anions in super-intense laser fields

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
$I^{crit}\left(10^{16}\ \frac{W}{cm^2}\right)$	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
$I^{max}\left(10^{16}\ \frac{W}{cm^2}\right)$	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.

Do atoms in superintense laser fields behave like diatomic molecules ?

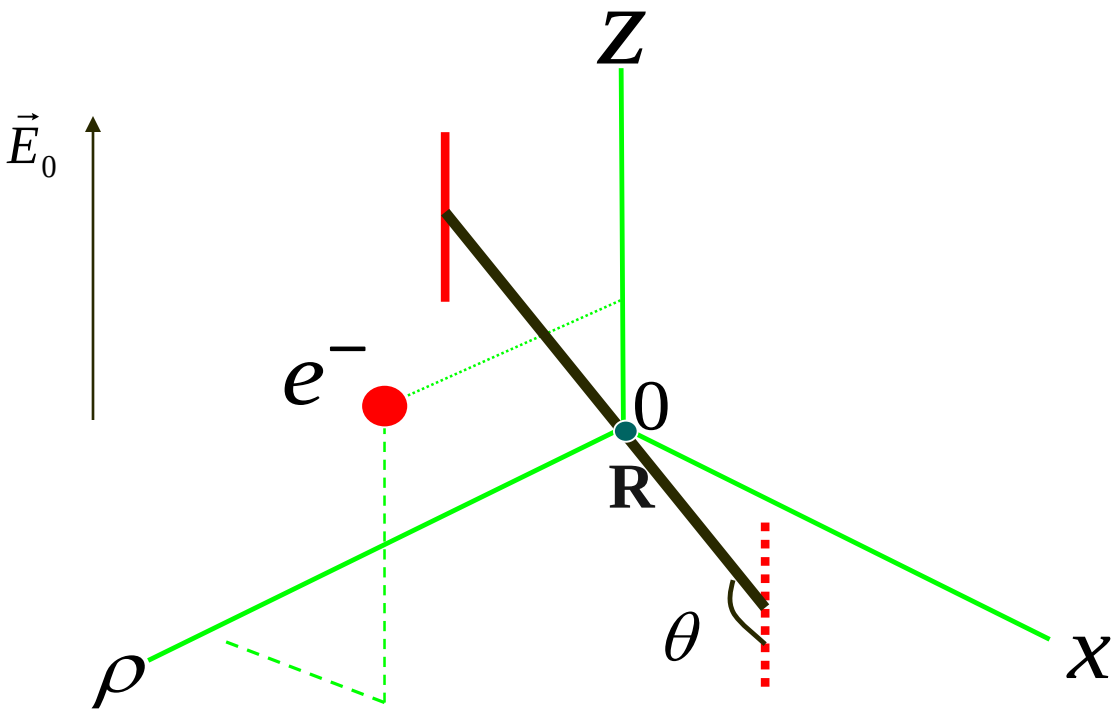


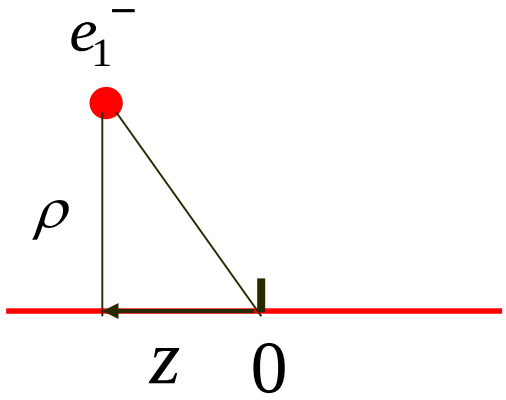
Large-D stability of molecules in linearly polarized superintense laser field

$$H = \frac{1}{2}\frac{1}{\rho^2} + V_{0,1}(\rho, z) + V_{0,2}(\rho, z) + \frac{\xi}{R}$$

$$V_{0,1}(\rho, z) = -\frac{1}{2\pi}\int_0^{2\pi} \frac{d\phi}{\sqrt{\rho^2 + (x - \frac{R}{2}\sin\theta)^2 + (z - \frac{R}{2}\cos\theta + \alpha_0 Sin\phi)^2}}$$

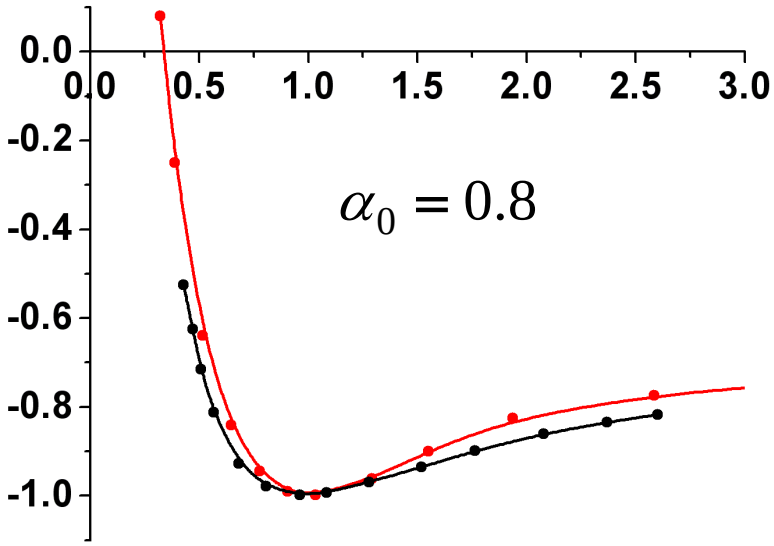
$$V_{0,2}(\rho, z) = -\frac{1}{2\pi}\int_0^{2\pi} \frac{d\phi}{\sqrt{\rho^2 + (x + \frac{R}{2}\sin\theta)^2 + (z + \frac{R}{2}\cos\theta + \alpha_0 Sin\phi)^2}}$$

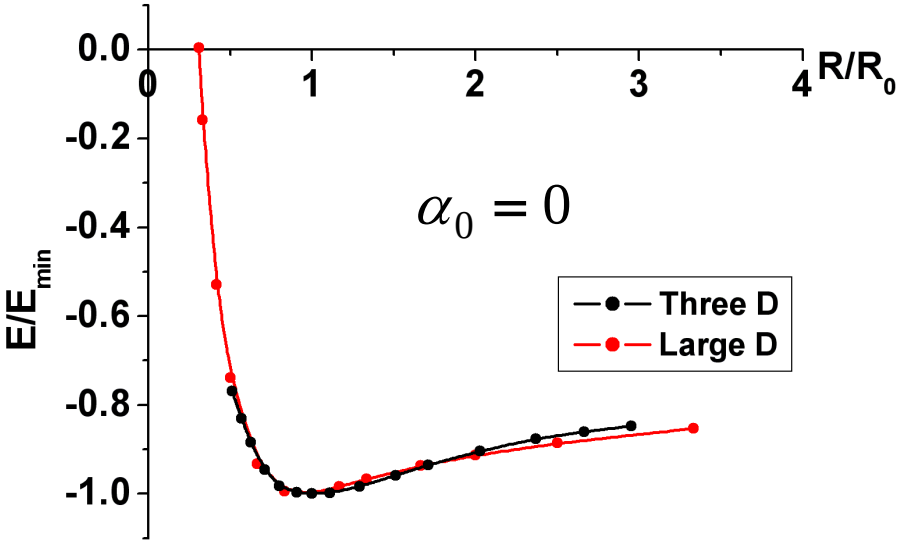


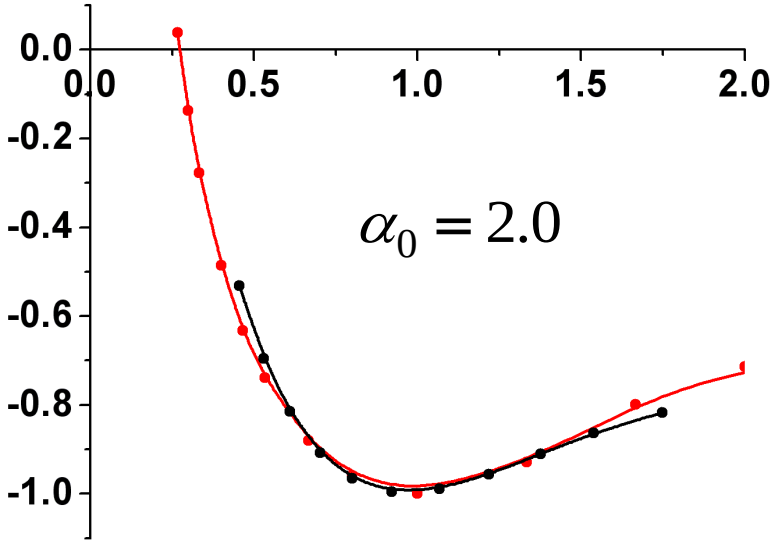


H_2^+

The laser polarization along the molecular axis (θ=0)

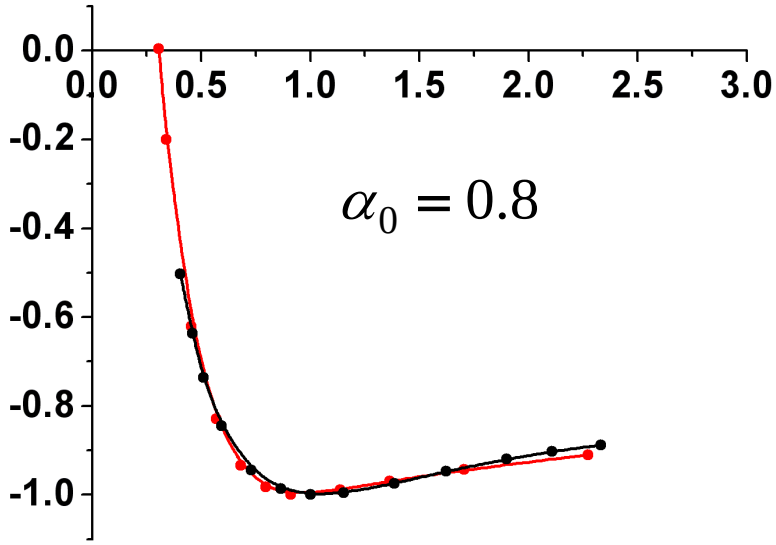


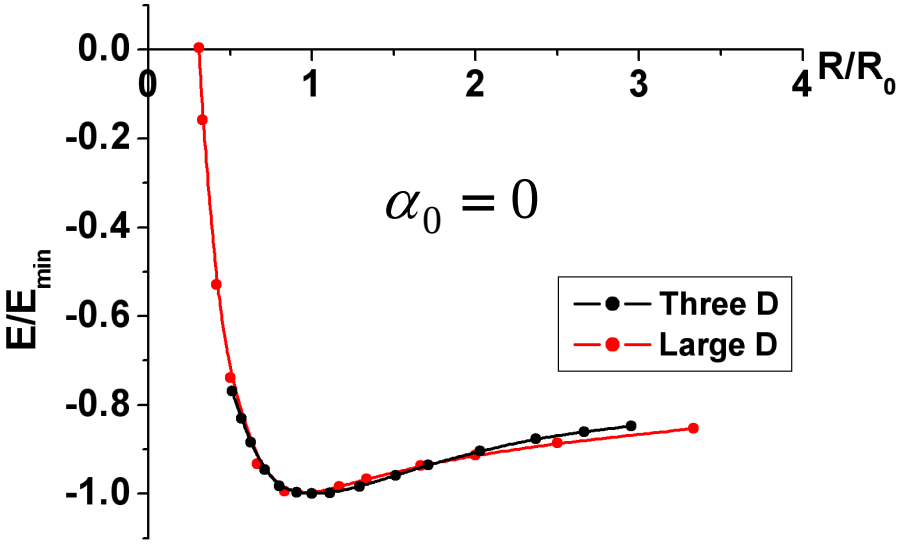


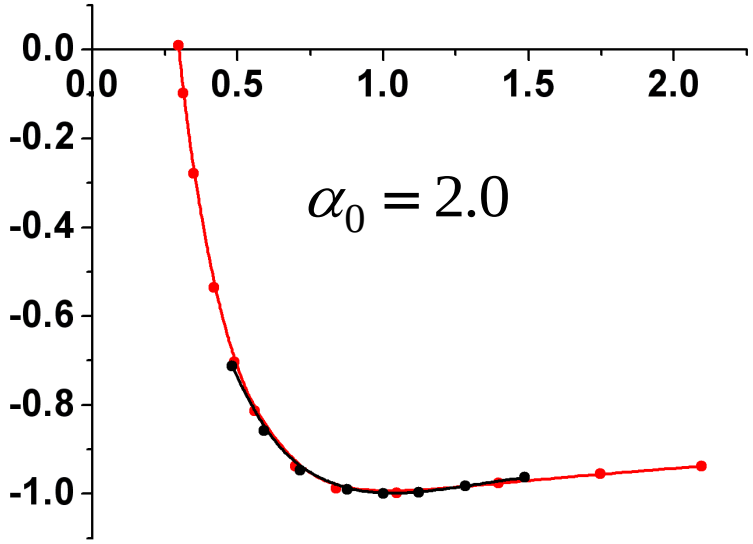


H_2^+

The laser polarization is vertical to the molecular axis (θ=90)







At the D→∞ limit

As per D-Scaling method:

$$H = \sum_{i=1}^{N} \frac{1}{2}\left(\frac{1}{\left(x_i^{\,2} + y_i^{\,2}\right)}\right) + \sum_{i=1}^{N} V_0(x_i, y_i, z_i) + \sum_{i=1}^{N}\sum_{j>i}^{N}\left(\frac{1}{\sqrt{\left(x_i - x_j\right)^2 + \left(y_i - y_j\right)^2 + \left(z_i - z_j\right)^2}}\right)$$

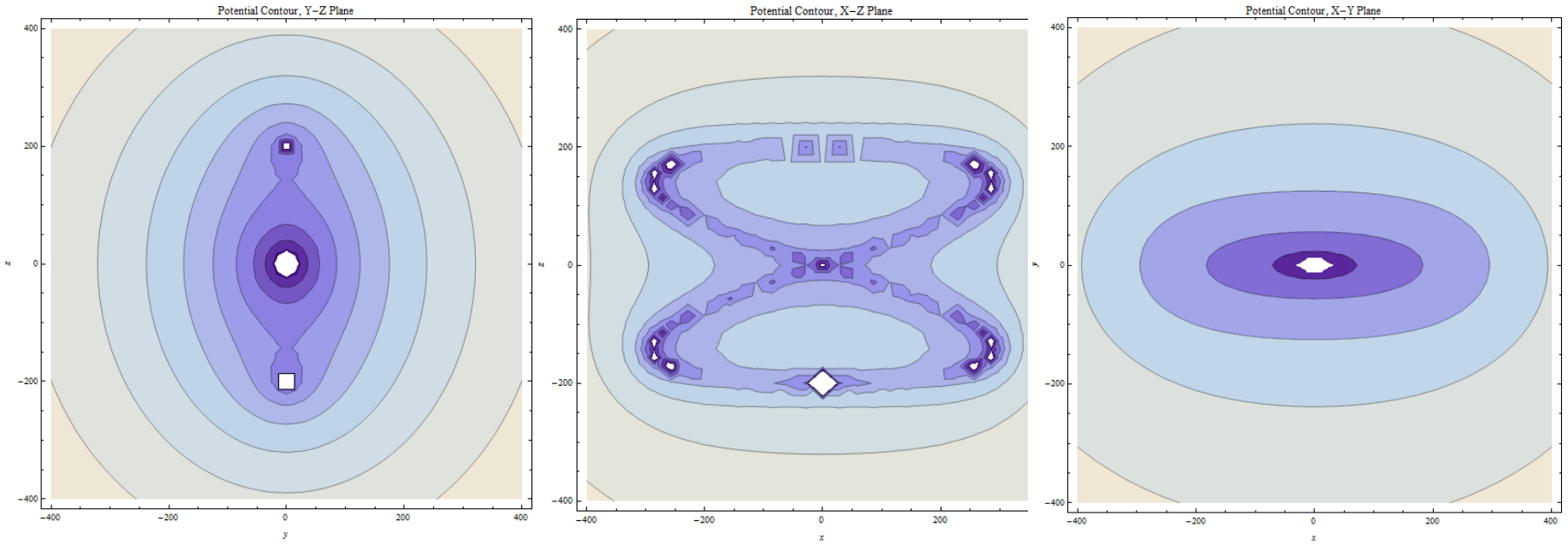
$$V_0(x, y, z) = \left(\frac{q}{2\pi}\right)\int_0^{2\pi} \frac{d\varphi}{\sqrt{\left(z + d * \cos(\varphi)\right)^2 + \left(y\right)^2 + \left(x - \frac{d^2}{\alpha}\sin(2\varphi)\right)^2}}$$

$$d = \frac{\nu}{2}$$

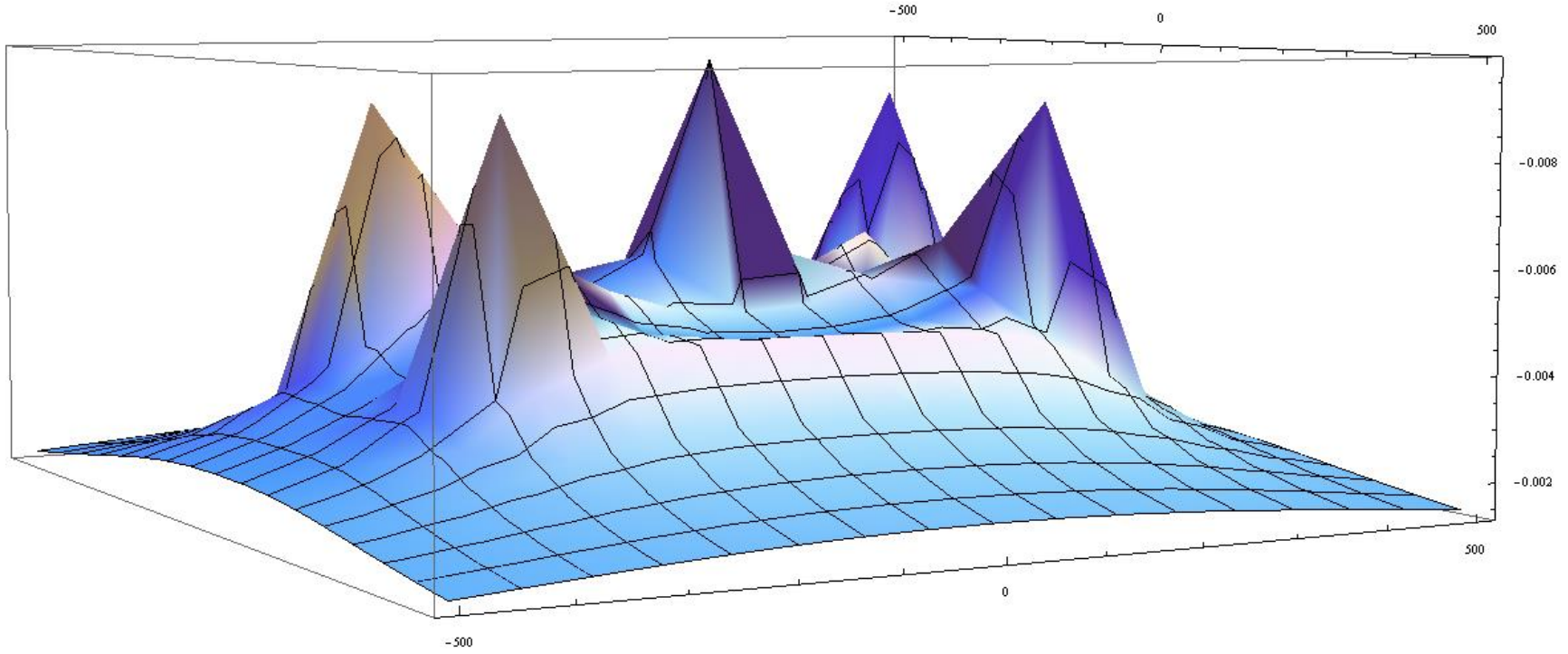
This is the problem to be minimized

Our Potential

- Potential generated by application of Relativistic Trajectory in HFFT
- v = 400



Alternate View



Trajectory

- The new relativistic trajectory used:

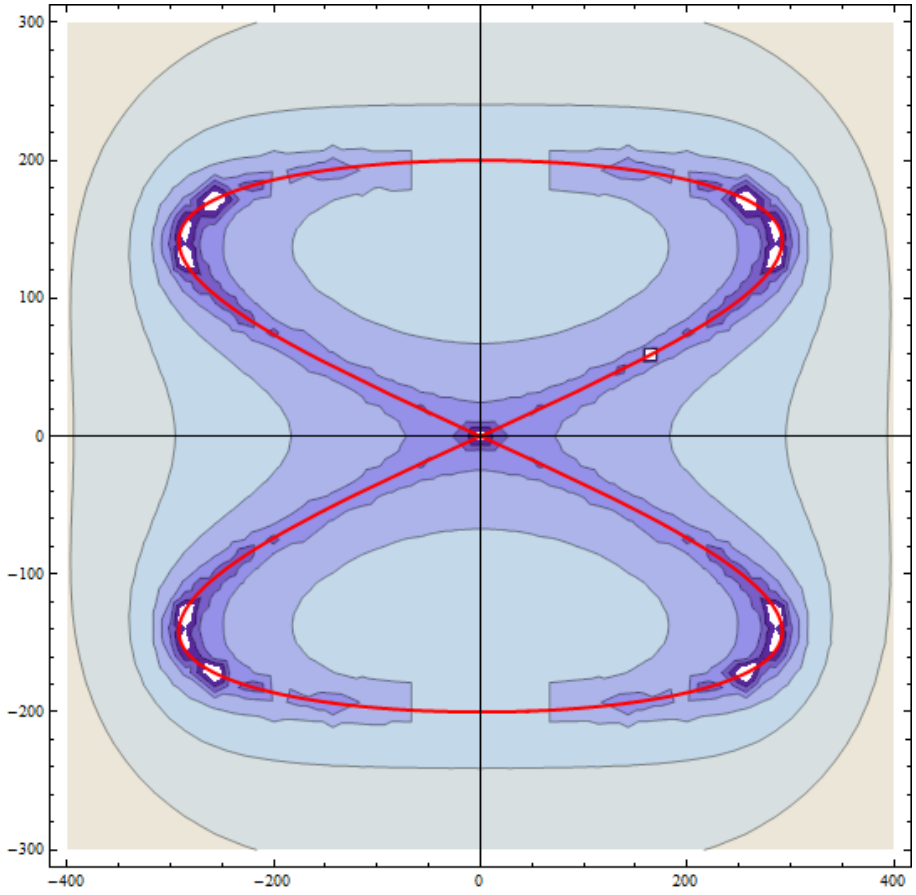
$$\alpha_{rel}(t) = \alpha_0\left(x_i \cos(\omega t) - x_j(\alpha_0\alpha_{fine})\sin(2\omega t)\right), \quad where\, x_i \perp x_j$$

- This trajectory was used within the HFFT potential, and the potential traces the equivalent parametric equation:

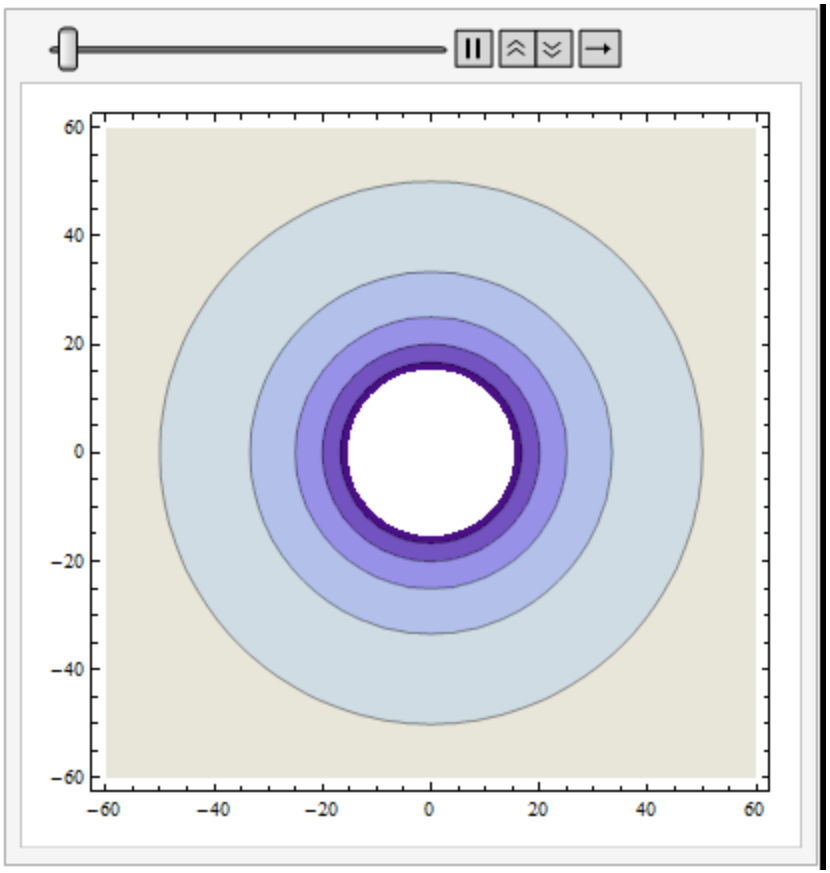
$$\left\{d^2\alpha_{fine}\sin(2t), 0, d\cos(t)\right\}, \quad t = (0, 2\pi)$$

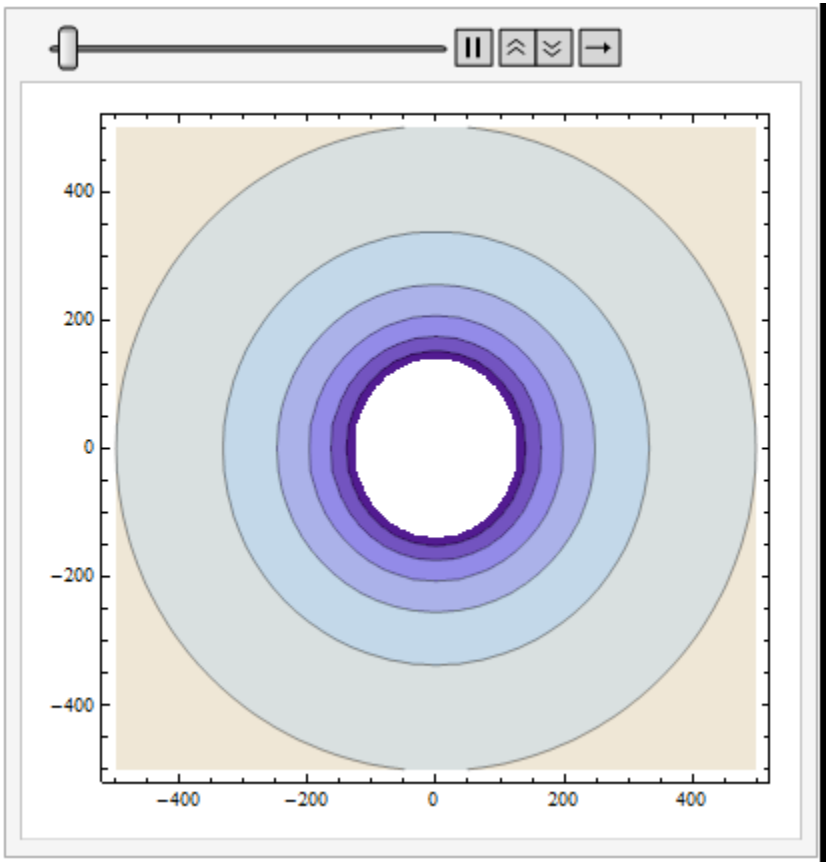
$$d = \alpha_0 = \nu/2$$

- The curve reaches it's maximum at t=π/4; the potential and electron density reach their extremes as well



Morphology


60
40
20
0
−20
−40
−60
−60
−40
−20
0
20
40
60


400
200
0
−200
−400
−400
−200
0
200
400

Summary

Symmetry breaking of electronic structure configurations resemble classical phase transitions

Quantum phase transitions can be used to explain and predict the stability of atoms, molecules and quantum dots.

Atomic dianions are unstable in the gas phase

Multiply charged negative ions are stable in superintense laser fields
(Intensity > 1 a.u. ~ 10^{16} W/cm^2)

Future Work

Combining FSS with Ab Initio and DFT

Combining FSS with Finite Element Methods

New Classification of Chemical Reactions

FSS and Efimov Systems

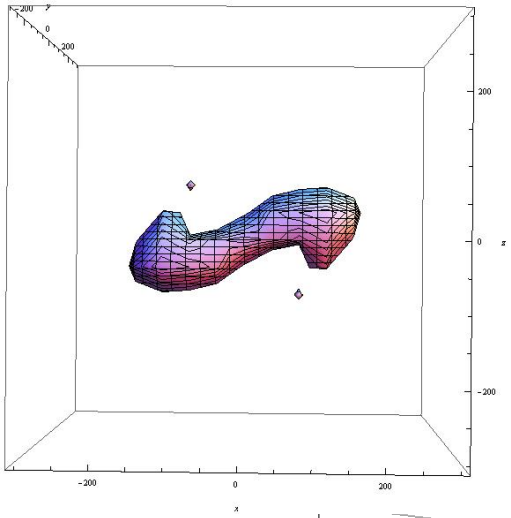
Stability of Matter in Superintese Laser Fields

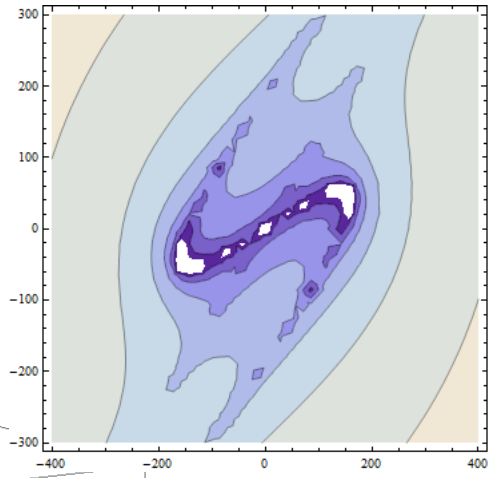
For more details See the review article:

- Sabre Kais and Pablo Serra, "Quantum Critical Phenomena and Stability of Atomic and Molecular Ions", Int. Rev. Phys. Chem. Vol 19, 97-121 (2000).
- S. Kais and P. Serra, "Finite Size Scaling for Atomic and Molecular Systems", Advances in Chemical Physics, Volume 125, 1-100 (2003).

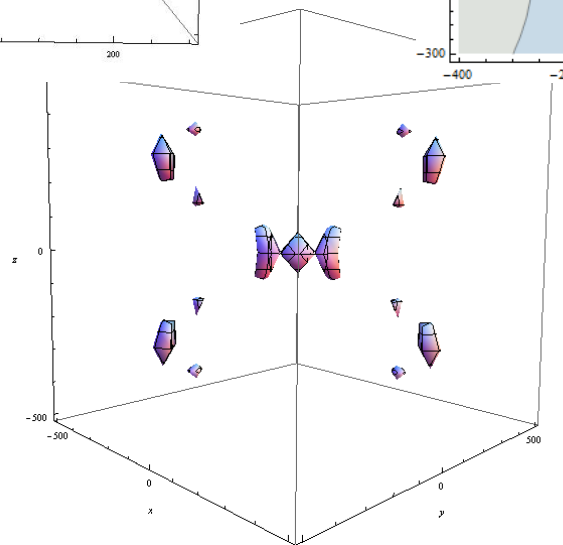
Further Directions

Combinations of linearly polarized lasers can deliver more exotic potentials with the chance of binding even more electrons.





Two lasers fired in the Y direction, linearly polarized in the X and Z directions



Two lasers fired, in the X and Y directions, both polarized in the Z

Efimov States

Efimov State is a quantum mechanical stable bound state of three particles, with any two particle subsystem is unstable. It was proposed by Vitaly Efimov in 1970 theoretically and was observed experimentally in 2006 for ultracold gas of caesium atoms.

Remove any one ring and the other two will fall apart.

Letter to: *Nature* **440**, 315-318 (16 March 2006)

Evidence for Efimov quantum states in an ultracold gas of caesium atoms

T. Kraemer, M. Mark, P. Waldburger, J. G. Danzl, C. Chin, B. Engeser, A. D. Lange, K. Pilch, A. Jaakkola, H.-C. Nägerl and R. Grimm

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Thank You!