Jellium Calculations for Large Metal Clusters
and their Semiclassical Interpretation

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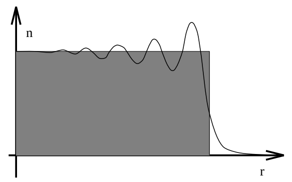
Homogeneous Jellium Model



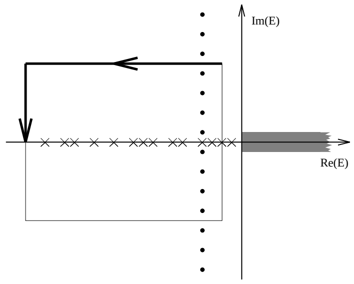
using Green's function

$$n(r) = \frac{1}{2\pi i}\oint G(r,r;E)\,dE$$
$$\sum \varepsilon_i = \int d^3r\,\frac{1}{2\pi i}\oint E\,G(r,r;E)\,dE$$

$\rightsquigarrow$ effort independent of number of states

to avoid poles on real axis and fluctuations in occupation

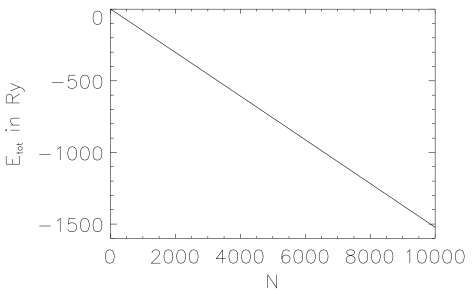
use finite T $\rightsquigarrow$ Matsubara Poles



Jellium Results: $E(N)$

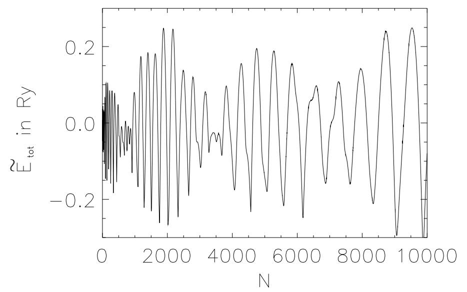
(plots show energy for Na jellies; data in /home/r2/koch/pvwave/jellium/Na.lda/conv.lda.00001-10000)

$E(N)$: total energy as function of cluster size



$\sim 10^3 Ry$

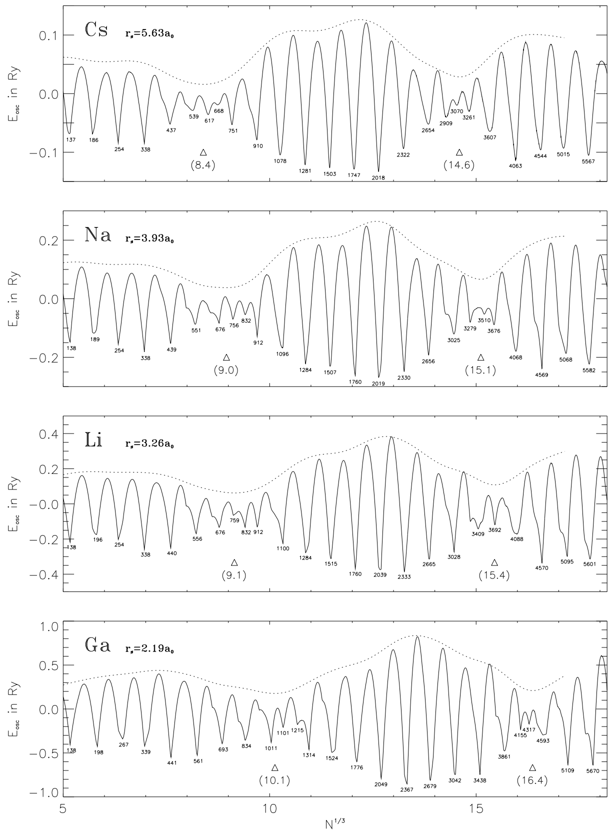
Subtracting smooth part $\bar{E}(N) = a_1\,N + a_2\,N^{2/3} + a_3\,N^{1/3}$ leaves $\tilde{E}(N)$:



$\sim 10^{-1} Ry$

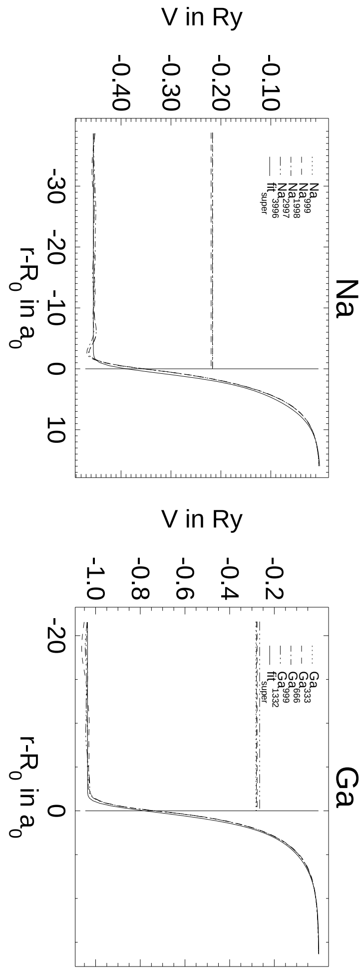
$\rightsquigarrow$ oscillations (**shells**)
& beating pattern (**supershells**)

Jellium Results: $\tilde{E}$ for $N_{el} = 125\ldots6000$



Jellium Results: Selfconsistent Potentials for different cluster sizes

potentials for clusters with approx. 1000, 2000, 3000, and 4000 electrons



⇝ potentials can easily be parametrized

Fit Selfconsistent Potentials:

Jellium potentials simply grow with $N^{1/3}$ without changing their shape too much.

⇝ fit selfconsistent potentials with modified Saxon-Woods Potential:

$$V(r,N) = \frac{-V_0}{1+\exp\left((r-R_0)/a(r)\right)}$$

where $R_0 = r_0 N^{1/3}$ (volume)

$a(r) = a_0 + a_1 \tanh(a_2(r-R_0))$ (surface)

i.e.: bulk density defines natural length scale $r_0 \approx r_s$
surface introduces a length scale a

⇝ *a/r_s should be a characteristic constant for the cluster problem* (cf. Reynolds number in hydrodynamics)

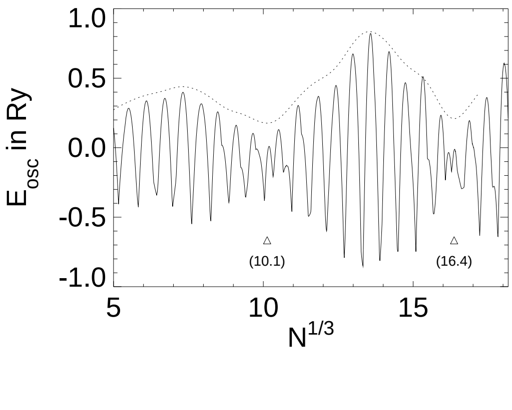
fitparameters:

material	V_0	r_0	a_0	a_1	a_2
Al	1.13	2.12	0.98	1.15	0.21
Ga	1.04	2.25	1.02	1.13	0.22
In	0.90	2.47	1.09	1.11	0.23
Tl	0.86	2.55	1.11	1.10	0.24
Li	0.59	3.34	1.35	1.09	0.27
Na	0.46	4.04	1.53	1.12	0.28
K	0.35	5.00	1.73	1.20	0.26
Rb	0.32	5.35	1.80	1.23	0.26
Cs	0.29	5.78	1.88	1.28	0.25

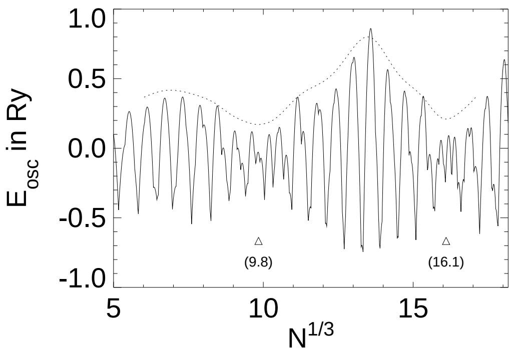
Rem.: Friedel oscillations for large-r_s materials **not** described

Example: $\tilde{E}$ for Gallium Clusters

Jellium Result

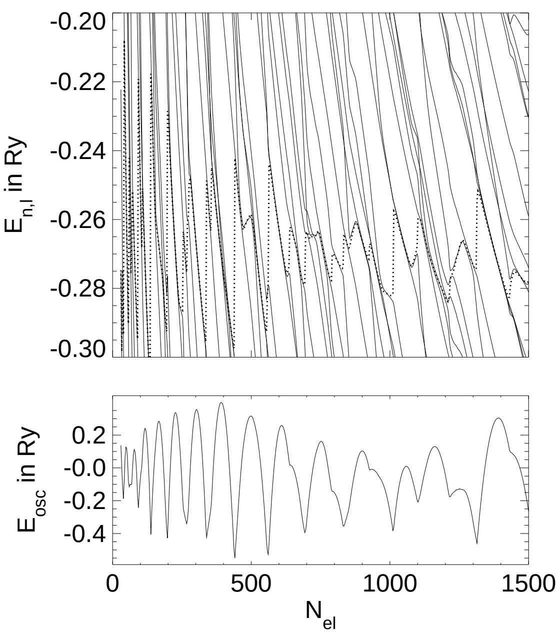


using fitpotential



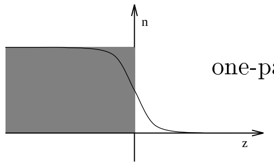
Jellium Results: Coulomb-Smoothing

one electron levels for gallium clusters



Estimate Selfconsistent Potential at Surface

Thomas-Fermi calculations are usually *the* choice to find out *qualitative* features



one-parameter trial density
$n(z) = n_I\, f(z/a)$

Energy Functional: J. R. Smith, PR **181**, 522-529 (1969)

- Thomas-Fermi kinetic energy & Kirzhnits gradient correction
- exchange energy (& $X\alpha$ correlation energy)
- Coulomb energy

minimize surface energy

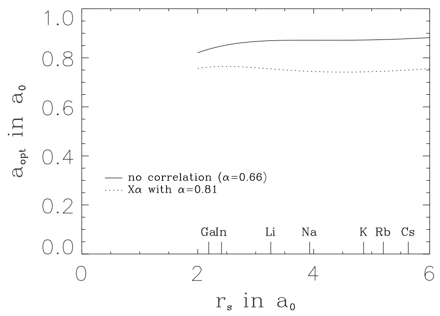
$$\sigma(a) = \int_{-\infty}^{\infty} \left\{ E[n(z)]\, n(z) - E[n_I\Theta(-z)]\, n_I\Theta(-z) \right\} dz$$

$\rightsquigarrow$ quadratic equation for a^2

example: $f(x) = \begin{cases} 1 - \frac{1}{2}e^{x} & ,\ x < 0 \\ \frac{1}{2}e^{-x} & ,\ x \geq 0 \end{cases}$

(Smith density)

Width of the Surface Region



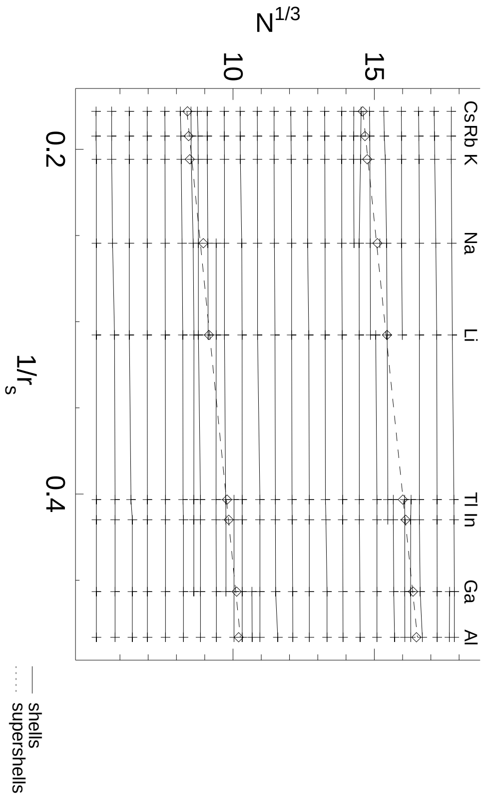
similar for other choices of $f(x)$

i.e.: a defines a length scale independent of r_s

$$\boxed{\frac{a}{r_s} \propto \frac{1}{r_s}}$$

i.e.: shells and supershells should scale with $1/r_s$!

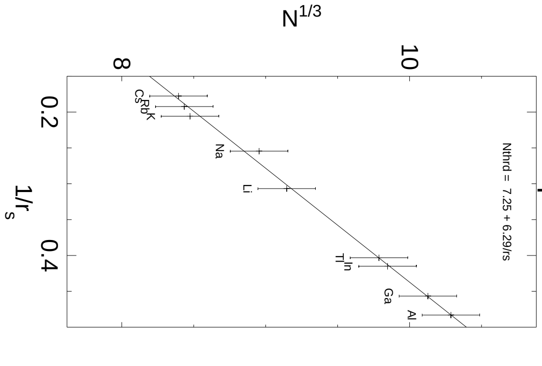
Scaling of Shells and Supershells with r_s



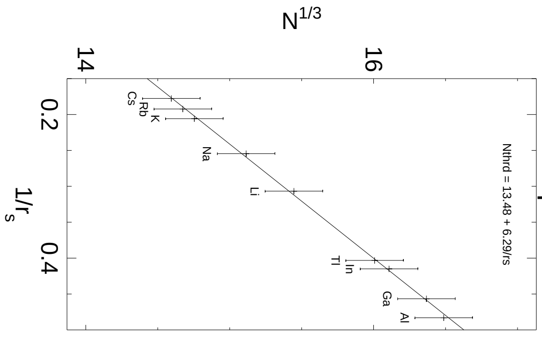
$\rightsquigarrow$ shells nearly unshifted; **linear** shift of supernodes

Jellium Results: Position of SuperNodes as Function of Jellium-Density

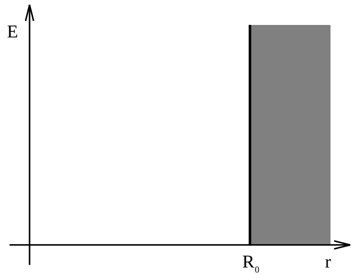
1st supernode



2nd supernode



Spherical Cavity:



$$-\frac{\hbar^2}{2m}\,\frac{d^2}{dr^2}\phi(r) = E\phi(r) \quad ; \qquad \phi(R_0) = 0$$

transformation: $x = r/R_0$

$$-\frac{\hat{\hbar}^2}{2m}\,\frac{d^2}{dx^2}\hat{\phi}(x) = E\hat{\phi}(x) \quad ; \qquad \hat{\phi}(1) = 0$$

$$\text{where } \hat{\hbar} = \frac{\hbar}{R_0}$$

i.e.: $R_0 \to \infty \qquad \hat{=} \qquad \hat{\hbar} \to 0$

$\rightsquigarrow$ **semiclassics**

Semiclassics: Periodic Orbit Expansion

Density of States:

$$\rho(E) = -\frac{1}{\pi}\,\mathrm{Im}\ \mathrm{Tr}\ G^+(r'', r'; E)$$

Path Integral approach: (for time-independent problems)

(evaluation of integrals for $\hbar \to 0$ by Method of Stationary Phase)

$$G(r'', r'; t) = \int \mathcal{D}[r]\ e^{i/\hbar\ S[r]}$$

$\Big\downarrow\ \hbar \to 0$ saddle-point: $\delta S[r] = 0$ (classical path); Caustic: $\delta^2 S[r] = 0$

$$\sum_{\text{classical paths } r(t)} \sqrt{\text{Density of paths around } r(t)}\ e^{i/\hbar\ S[r] + \text{Morse-Phase}}$$

$\Big\downarrow$ Fourier Transformation   classical path $r' \xrightarrow{t} r''$ $\forall E$; classical path $r' \xrightarrow{E} r''$ $\forall t$

$$G(r'', r'; E) = \sum_{\text{classical paths } r(E)} \sqrt{\Delta}\ e^{i/\hbar\ S[r] + \text{Maslov-Phase}}$$

$\Big\downarrow\ r'' \to r'$ paths closed in configuration-space, i.e.: $\vec{r}(T) = \vec{r}(0)$

direct path $\quad + \quad$ closed paths

$\Big\downarrow\ \int d^3r$ $0 \stackrel{!}{=} \frac{\partial S_{r',r'}}{\partial r'} = \lim_{r'' \to r'} \left(\frac{\partial S_{r',r''}}{\partial r'} - \frac{\partial S_{r',r''}}{\partial r''} \right) = \lim_{r'' \to r'} (p' - p'')$

i.e.: paths closed in phase-space

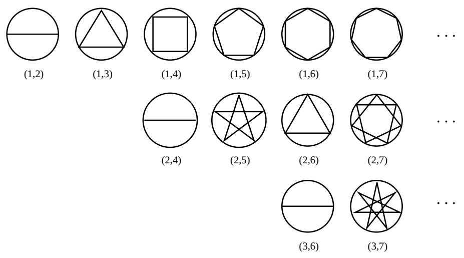
Thomas-Fermi term $\quad + \quad$ periodic orbits

$$\rightsquigarrow \quad \boxed{\rho(E) = \bar{\rho}(E) + \tilde{\rho}(E)}$$

Periodic Orbits (λ, ν) for a Spherical Cavity

λ : number of turns

ν : number of vertices



Gutzwiller Formula for radially symmetric problems:

J.Math.Phys. **11**, 1791-1806 (1970), formula (43)

$$\tilde{G}_{(\lambda,\nu)}(r, r; E) \;=\; -i\,\sqrt{\frac{2}{\pi}}\,\frac{L}{\hbar^2}\,\left|2\nu\frac{\partial\phi}{\partial L/\hbar}\right|^{-1/2}\,\frac{m/r^2}{\sqrt{2m(E - V(r)) - L^2/r^2}}$$

$$\times\ \exp\left(i\left(S/\hbar - (\phi_M \nu + \lambda - 1/4)\pi\right)\right)$$

S	$=$	$2\nu s = 2\nu(s_r + L\phi)$	total action
s_r	$=$	$\int_{r_{in}}^{r_{out}} \sqrt{2m(E - V(r)) - L^2/r^2}\, dr$	radial action
ϕ	$=$	$\int_{r_{in}}^{r_{out}} \frac{L/r^2\ dr}{\sqrt{2m(E - V(r)) - L^2/r^2}}$	turning angle

$$\rightsquigarrow \tilde{\rho}(E) \;=\; -\frac{1}{\pi}\sum_{(\lambda,\nu)} \mathrm{Im}\ 4\pi \int G^+_{(\lambda,\nu)}(r, r; E)\ r^2 dr$$

$$=\; \sum_{(\lambda,\nu)} A_{(\lambda,\nu)}\ \cos(\Lambda_{(\lambda,\nu)} kR_0 - \varphi_{(\lambda,\nu)})$$

Example: Spherical Cavity

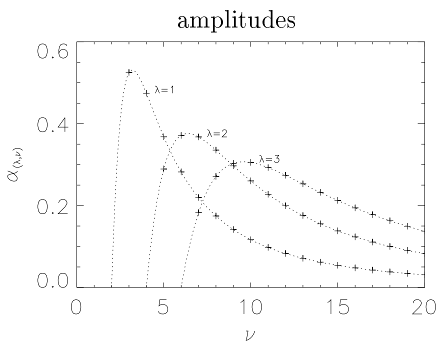
$$\bar{\rho}(E) \;=\; 2\,R_0^2\left(\frac{kR_0}{3\pi} - \frac{1}{4} + \frac{1}{3\pi kR_0}\right)$$

$$\tilde{\rho}(E) \;=\; \sqrt{k}\,R_0^{5/2} \sum_{(\lambda,\nu)} \alpha_{(\lambda,\nu)}\ \cos\left(\Lambda_{(\lambda,\nu)} kR_0 - \varphi_{(\lambda,\nu)}\right)$$

$$\Lambda_{(\lambda,\nu)} \;=\; 2\nu\ \sin\left(\frac{\pi\lambda}{\nu}\right) \qquad \propto \text{length of orbit}$$

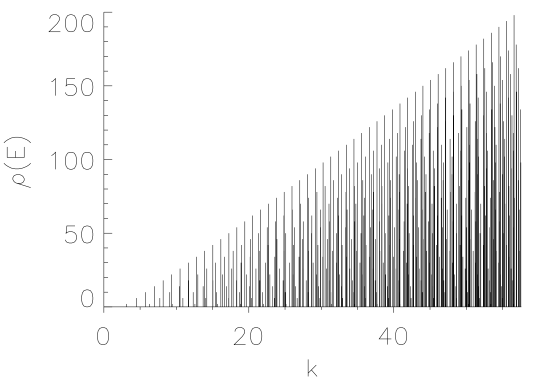
$$\varphi_{(\lambda,\nu)} \;=\; \left(\frac{3}{2}\nu + \lambda - \frac{1}{4}\right)\pi \qquad \text{Maslov phase}$$

$$\alpha_{(\lambda,\nu)} \;=\; 4\ \underbrace{\cos\left(\frac{\pi\lambda}{\nu}\right)}_{L}\ \underbrace{\sqrt{\frac{\sin\left(\frac{\pi\lambda}{\nu}\right)}{2\nu}}}_{|.|^{-1/2}}\ \underbrace{\sin\left(\frac{\pi\lambda}{\nu}\right)}_{\int d^3r}$$

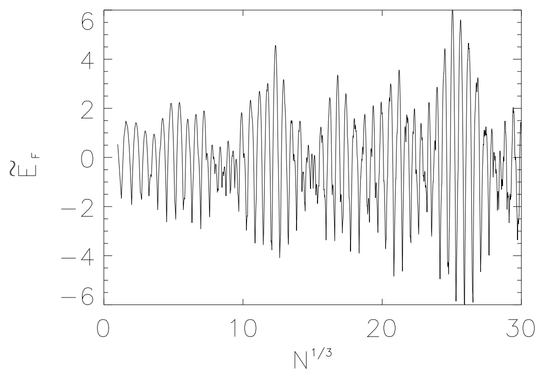


Spherical Cavity:

Density of States: δ-peaks



Oscillating Part of Total Energy: smooth curve



Find $\tilde{E}(N) = E(N) - \bar{E}(N)$:

$$\begin{array}{rcl} N &=& \int_0^{E_F} \rho(N;E)\, dE \\ N &=& \int_0^{\bar{E}_F} \bar{\rho}(N;E)\, dE \\ \hline\hline 0 &=& \int_0^{E_F} \tilde{\rho}(N;E)\, dE \\ && + \underbrace{\int_{\bar{E}_F}^{E_F} \bar{\rho}(N;E)\, dE}_{\approx (E_F - \bar{E}_F)\,\bar{\rho}(E_F)} \end{array} \qquad \begin{array}{rcl} E &=& \int_0^{E_F} E\,\rho(N;E)\, dE \\ \bar{E} &=& \int_0^{\bar{E}_F} E\,\bar{\rho}(N;E)\, dE \\ \hline\hline \tilde{E} &=& \int_0^{E_F} E\,\tilde{\rho}(N;E)\, dE \\ && + \underbrace{\int_{\bar{E}_F}^{E_F} E\,\bar{\rho}(N;E)\, dE}_{\approx (E_F - \bar{E}_F)\,E_F\,\bar{\rho}(E_F)} \end{array}$$

$$\rightsquigarrow \tilde{E}(N) \approx \int_0^{\bar{E}_F(N)} (E - \bar{E}_F(N))\,\tilde{\rho}(N;E)\, dE$$

$$= -\int_0^{E_F(N)} dE \int_0^{E} dE'\,\tilde{\rho}(N;E')$$

repeated integration by parts of

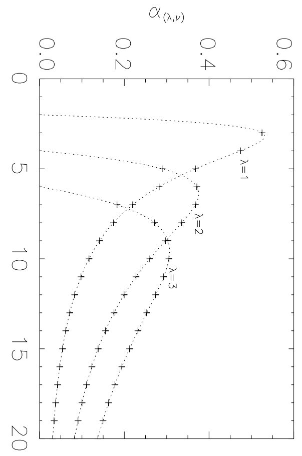
$$-\int_0^{\bar{k}_F} dk\, k \int_0^{k} dk'\, k^{3/2} \cos\left(\Lambda_{(\lambda,\nu)} k' R_0 + \varphi_{(\lambda,\nu)}\right)$$

gives asymptotic expansion in powers of $\Lambda_{(\lambda,\nu)} R_0$:

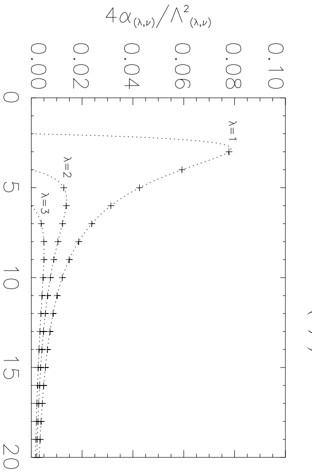
$$\tilde{E}(N) = \bar{k}_F^{5/2} \sqrt{R_0} \sum_{(\lambda,\nu)} \frac{4\alpha_{(\lambda,\nu)}}{\Lambda^2_{(\lambda,\nu)}} \cos\left(\Lambda_{(\lambda,\nu)} \bar{k}_F R_0 - \varphi_{(\lambda,\nu)}\right)$$

Convergence of the Periodic Orbit Expansion

$\tilde{\rho}$: $\alpha(\lambda,\nu)$



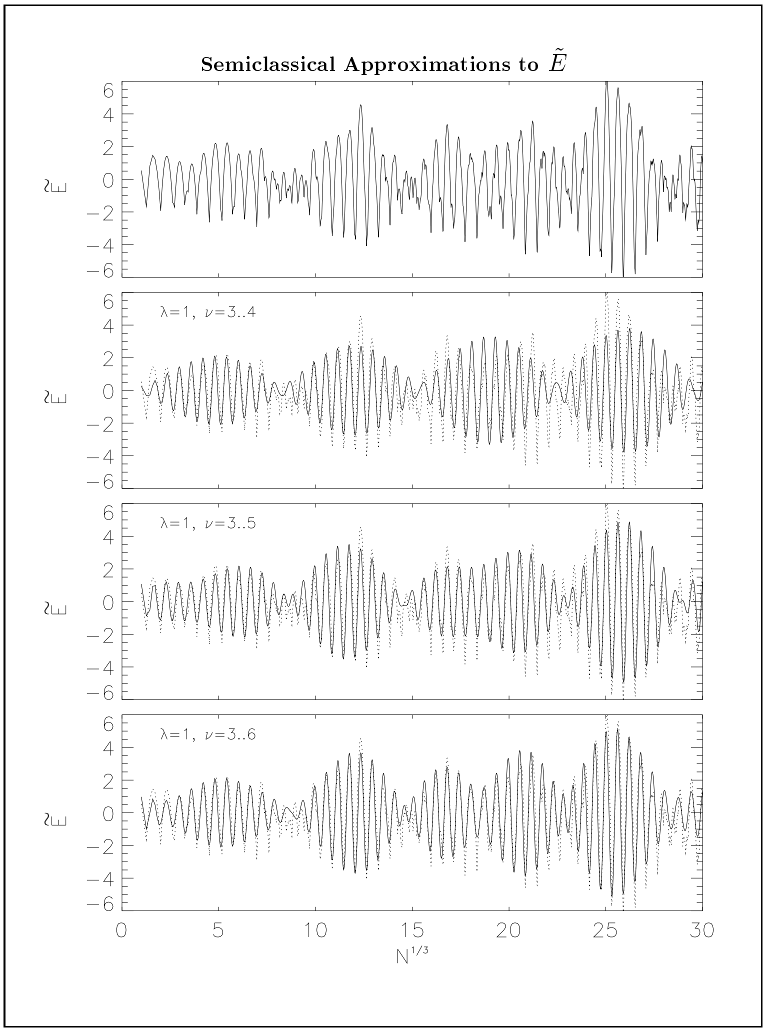
$\tilde{E}$: $\beta(\lambda,\nu) = \frac{4\alpha_{(\lambda,\nu)}}{\Lambda^2_{(\lambda,\nu)}}$

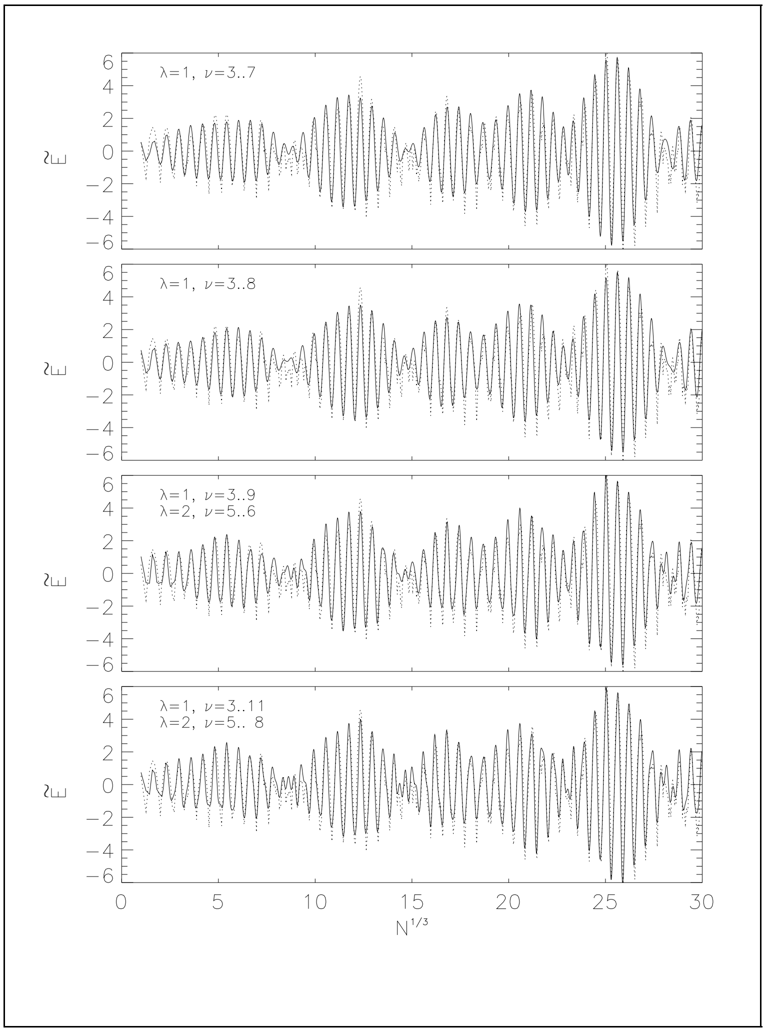


Being an integrated quantity, $\tilde{E}$ is smoother than $\tilde{\rho}$, thus the longer orbits, which determine the function on a smaller scale than the short ones, contribute less. The maximum contribution of an oscillating function to an integral is the area under one half wave — which decreases as the frequency increases. Thus the integrations from $\tilde{\rho}$ to $\tilde{E}$ damp the higher frequencies (longer orbits).

Longer orbits are less important for $\tilde{E}$ than for $\tilde{\rho}$.

$\rightsquigarrow$ damping without k_i

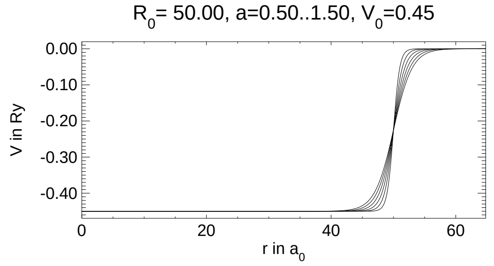

Semiclassical Approximations to $\tilde{E}$
$\tilde{E}$
λ=1, ν=3..4
λ=1, ν=3..5
λ=1, ν=3..6
$N^{1/3}$


λ=1, ν=3..7
λ=1, ν=3..8
λ=1, ν=3..9
λ=2, ν=5..6
λ=1, ν=3..11
λ=2, ν=5.. 8
$\tilde{E}$
$N^{1/3}$

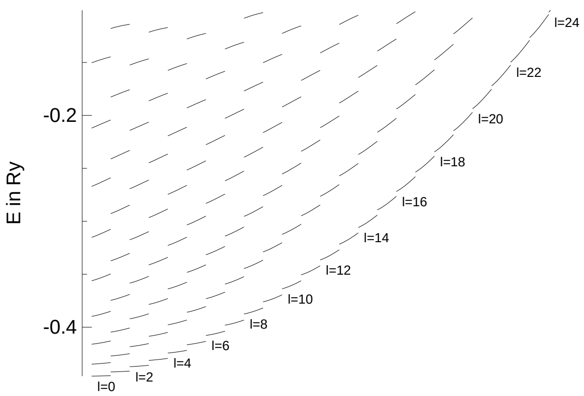
Saxon-Woods Potential:

$$V(r) = \frac{-V0}{1 + exp\left((r - R_0)/a\right)}$$

potential corresponds for $a \approx 1.0$ to a Na_{2060} cluster (data from semifit)
other materials: $a_{here}^{mat} = a_{mat} r_s^{Na}/r_s^{mat}$ range from $a_{here}^{Cs} \approx 0.55$ to $a_{here}^{Al} \approx 1.65$

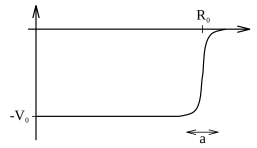


shift of levels $\varepsilon_{n,l}$ with surface parameter a



Semiclassics for more realistic potentials

relevant parameters of cluster potentials:



$$\begin{array}{lcll} R_0(N) & = & r_s N^{1/3} & : \text{ width of the well} \\ a(N) & \equiv & a & : \text{ width of the surface} \\ V_0(N) & \equiv & V_0 & : \text{ depth of the well} \end{array}$$

$$\tilde{E} = \sum_{(\lambda,\nu)} B_{(\lambda,\nu)} \; \cos\left(S_{(\lambda,\nu)}/\hbar - \varphi_{(\lambda,\nu)}\right)$$

Changing the potential changes:

(i) orbit condition (determines $L_{(\lambda,\nu)}$)

$$\phi_{(\lambda,\nu)} = \int_{r_{in}}^{r_{out}} \frac{L/r^2 \; dr}{\sqrt{2m(E - V(r)) - L^2/r^2}} \stackrel{!}{=} \frac{\pi\lambda}{\nu}$$

(ii) classical action

$$S_{(\lambda,\nu)} = 2\nu \int_{r_{in}}^{r_{out}} \sqrt{2m(E - V(r)) - L^2/r^2}\, dr + 2\nu \; L \; \phi_{(\lambda,\nu)}$$

(iii) Fermi energy

$$k_F r_s = \left(\frac{9\pi}{4}\right)^{1/3} + c_S \, N^{-1/3} + c_C \, N^{-2/3} + \ldots$$

(iv) Maslov phase $\quad \varphi_{(\lambda,\nu)}$

(v) amplitudes

$$B_{(\lambda,\nu)} = \frac{16 m\hbar}{\sqrt{\pi\nu}} \, \frac{L_{(\lambda,\nu)}}{\hbar} \left|\frac{\partial\phi}{\partial L/\hbar}\right|^{-1/2} \int_{r_{in}}^{r_{out}} \frac{dr}{\sqrt{2m(E_F - V(r)) - L^2_{(\lambda,\nu)}/r^2}} \, \frac{\bar{k}_F^4}{S^2_{(\lambda,\nu)}}$$

fundamental integral:

$$s_r = \int_{r_{in}}^{r_{out}} \sqrt{2m(E_F - V(r)) - L^2/r^2}\, dr$$

Idea: expand around cavity limit $a = 0$

$$V(r) = -V_0 + \Delta V(r)\;; \quad \Delta V(r) = -V_0\, f(a;r)$$

$$\text{e.g.: } V(r) = \frac{-V_0}{1 + e^{(r-R_0)/a}} = -V_0 + \frac{V_0}{1 + e^{-(r-R_0)/a}}$$

$$\rightsquigarrow s_r = pR_0 \underbrace{\int_{\hat{r}_{in}}^{\hat{r}_{out}} \sqrt{1 + \hat{f}(\hat{a};\hat{r})/P^2 - \hat{L}^2/\hat{r}^2}\, d\hat{r}}_{\hat{s}_r(\hat{L}, P, \hat{a})}$$

where $\hat{r} = \frac{r}{R_0}, \quad \hat{a} = \frac{a}{R_0}, \quad \hat{L} = \frac{L}{pR_0}, \quad P = \sqrt{\frac{E + V_0}{V_0}}$

other integrals follow by differentiation, e.g.:

$$\phi = \int_{r_{in}}^{r_{out}} \frac{L/r^2 \; dr}{\sqrt{2m(E - V(r)) - L^2/r^2}} = -\frac{\partial}{\partial \hat{L}} \hat{s}_r$$

Ansatz:

$$\begin{aligned} \hat{s}_r(\hat{L}, P, \hat{a}) \;&=\; \hat{s}_r^{cavity}(\hat{L}) \;+\; \delta\hat{s}_r(\hat{L}, P, \hat{a}) \\ \hat{L}_{(\lambda,\nu)} \;&=\; \hat{L}^{cavity}_{(\lambda,\nu)} \;+\; \delta\hat{L}_{(\lambda,\nu)}(P, \hat{a}) \end{aligned}$$

$$\begin{aligned} \rightsquigarrow \hat{s}_{(\lambda,\nu)}(P, \hat{a}) \;&=\; \hat{s}_r(\hat{L}_{(\lambda,\nu)}, P, \hat{a}) + \hat{L}_{(\lambda,\nu)}\, \phi \\ &=\; \hat{s}^{cavity}_{(\lambda,\nu)} + \delta\hat{s}_r(\hat{L}_{(\lambda,\nu)}, P, \hat{a}) \end{aligned}$$

Thus we neither need to care about $\hat{L}_{(\lambda,\nu)}$, nor about $\delta\hat{s}$, but it is sufficient to consider $\delta\hat{s}_r$! (cancellation)

Linearization:

(motivated by scaling analysis of supernode positions!)

$$\boxed{\hat{s}_r \;=\; \hat{s}_r^{cavity}(\hat{L}) \;+\; \hat{I}_s(\hat{L}, P)\; \hat{a} \;+\; \mathcal{O}(\hat{a}^2)}$$

classical action:

$$\begin{aligned} S_{(\lambda,\nu)}/\hbar \;&=\; 2\nu\hat{s}\;\; k_F r_s \;\; N^{1/3} \\ &=\; 2\nu \left(\tfrac{9\pi}{4}\right)^{1/3} \hat{s}^{cavity}_{(\lambda,\nu)} \; N^{1/3} && \text{oscillation} \\ &\quad + 2\nu \left(\left(\tfrac{9\pi}{4}\right)^{1/3} I_s \, \tfrac{a}{r_s} + c_S \hat{s}^{cavity}_{(\lambda,\nu)}\right) && \text{phase shift} \\ &\quad + \mathcal{O}(N^{-1/3}) \end{aligned}$$

asymptotic expansion

$$k_F r_s = \left(\frac{9\pi}{4}\right)^{1/3} + \left(\frac{3\pi}{8} - c_S^{(0)}(P) - \left(\frac{9\pi}{4}\right)^{1/3} I_N(P)\, \frac{a}{r_s}\right) \; N^{-1/3} + \ldots$$

Maslov phase

$$\begin{aligned} \varphi_{(\lambda,\nu)} \;&=\; \left(\frac{3}{2}\nu + \lambda + \frac{1}{4}\right)\pi - 2\nu\Delta\varphi \\ \Delta\varphi(\hat{L}_{(\lambda,\nu)}, P) \;&=\; \arctan\sqrt{\frac{1}{P^2(1 - \hat{L}^2_{(\lambda,\nu)})} - 1} - \frac{\pi}{2} \end{aligned}$$

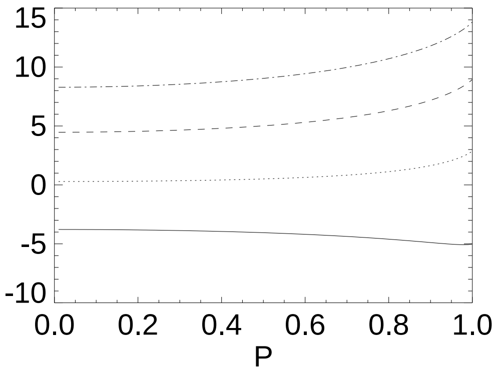
$$\begin{aligned} S_{(\lambda,\nu)}/\hbar - \varphi_{(\lambda,\nu)} \;=\;& S^{cavity}_{(\lambda,\nu)}/\hbar - \varphi^{cavity}_{(\lambda,\nu)} \\ & -2\nu \left(\frac{9\pi}{4}\right)^{1/3} \left[\hat{I}_N(P)\, \hat{s}^{cav}_{(\lambda,\nu)} - \hat{I}_s(\hat{L}^{cav}_{(\lambda,\nu)}, P)\right] \frac{a}{r_s} \\ & -2\nu \left(c_S^{(0)}(P)\, \hat{s}^{cav}_{(\lambda,\nu)} - \Delta\varphi(\hat{L}^{cav}_{(\lambda,\nu)}, P)\right) \end{aligned}$$

Results:

$$\hat{I}_s(\hat{L}_{(\lambda,\nu)},P) \;=\; \frac{2}{P}\left(P_{(\lambda,\nu)}\ln(2P_{(\lambda,\nu)}) - \sqrt{1-P_{(\lambda,\nu)}^2}\,\arcsin(P_{(\lambda,\nu)})\right)$$
$$\text{where } P_{(\lambda,\nu)} := P\,\sqrt{1-\hat{L}^2_{(\lambda,\nu)}}$$

$$\hat{I}_N(P) \;=\; 2\left(\ln(2P) - \frac{1}{P^2} + \left(\frac{1}{P^2}-1\right)^{3/2}\arcsin(P)\right)$$

$$\delta^{(a)}_{(\lambda,\nu)} = 2\nu\left(\tfrac{9\pi}{4}\right)^{1/3}\left[\hat{I}_N(P)\,\hat{s}^{cav}_{(\lambda,\nu)} - \hat{I}_s(\hat{L}^{cav}_{(\lambda,\nu)},P)\right]$$

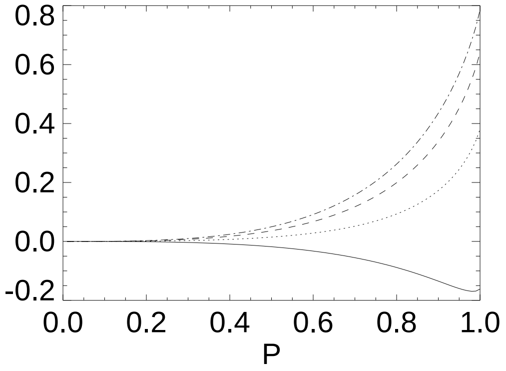


Results:

$$c_S^{(0)}(P) \;=\; \frac{3}{4}\left(\left(2-\frac{1}{P^2}\right)\arcsin(P) + \sqrt{\frac{1}{P^2}-1}\right)$$

$$\Delta\varphi(\hat{L}_{(\lambda,\nu)},P) \;=\; \arcsin(P_{(\lambda,\nu)})$$

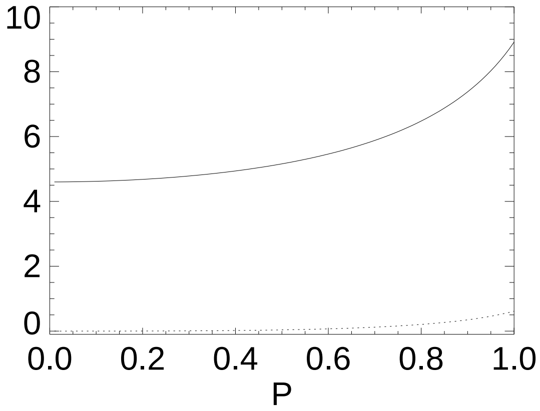
$$\delta^{(b)}_{(\lambda,\nu)} = 2\nu\left(c_S^{(0)}(P)\,\hat{s}^{cav}_{(\lambda,\nu)} - \Delta\varphi(\hat{L}^{cav}_{(\lambda,\nu)},P)\right)$$



Supernodes: minima in envelope of $\tilde{E}$

$$N_n^{1/3} = \frac{(2n+1)\pi \;+\; \left(\delta^{(a)}_{(1,4)} - \delta^{(a)}_{(1,3)}\right)\dfrac{a}{r_s} \;+\; \delta^{(b)}_{(1,4)} - \delta^{(b)}_{(1,3)}}{\left(\hat{S}_{(1,4)} - \hat{S}_{(1,3)}\right)\left(\frac{9\pi}{4}\right)^{1/3}}$$

supershell-period 7.11; supershell-shift:

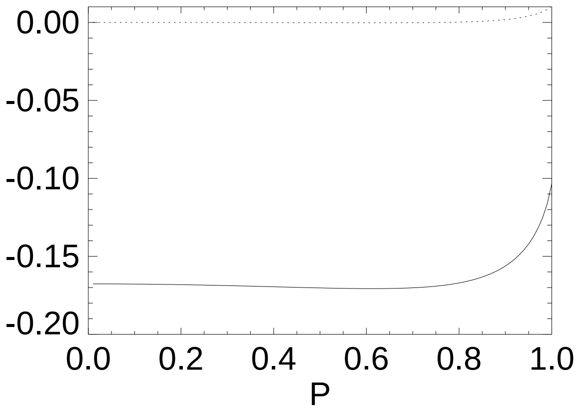


$\rightsquigarrow$ strong shift $\propto a/r_s$

Shells: minima in $\tilde{E}$

$$N_n^{1/3} = \frac{2(2n+1)\pi \;+\; \left(\delta^{(a)}_{(1,4)} + \delta^{(a)}_{(1,3)}\right)\dfrac{a}{r_s} \;+\; \delta^{(b)}_{(1,4)} + \delta^{(b)}_{(1,3)}}{\left(\hat{S}_{(1,4)} + \hat{S}_{(1,3)}\right)\left(\frac{9\pi}{4}\right)^{1/3}}$$

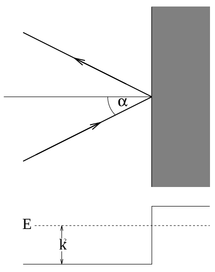
shell-period 0.60; shell-shift:



$\rightsquigarrow$ practically no shift

Maslov Phase: (assuming the limit $R_0 \to \infty$)

3d scattering phase:



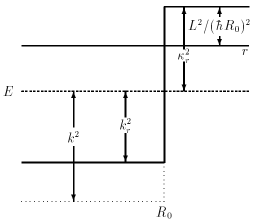
Ansatz:

$$\Psi(\vec{r}) = \begin{cases} \left(e^{i(k_x x+\delta)} + e^{-i(k_x x+\delta)}\right) & e^{i(k_y y+k_z z)}, x \le 0 \\ A\, e^{-\kappa_x x} & e^{i(k_y y+k_z z)}, x \ge 0 \end{cases}$$

where
$$k_x = k\cos(\alpha)$$
$$\kappa_x = \sqrt{2mV_0/\hbar^2 - k_x^2}$$

matching: $\boxed{\tan\delta = \frac{\kappa_x}{k_x}}$

semiclassical phase: radial potential shifts $V(R_0)$ upwards by $L^2/(\hbar R_0)^2$



Ansatz:

$$\Psi(\vec{r}) = \begin{cases} \cos\left(\int_r^{R_0} k_r(r)\,dr - \delta\right), & r \le R_0 \\ A\, e^{-\kappa_r r} & , r \ge R_0 \end{cases}$$

where
$$k_r = \sqrt{k^2 - L^2/(\hbar R_0)^2}$$
$$\kappa_r = \sqrt{2mV_0/\hbar^2 - k_r^2}$$

matching: $\boxed{\tan\delta = \frac{\kappa_r}{k_r}}$

Comparison for a cavity orbit (λ, ν):

geometry: $\cos(\alpha) = \quad \sin(\pi\lambda/\nu)$
orbit condition: $L_{(\lambda,\nu)} = \hbar k R_0\, \cos(\pi\lambda/\nu)$

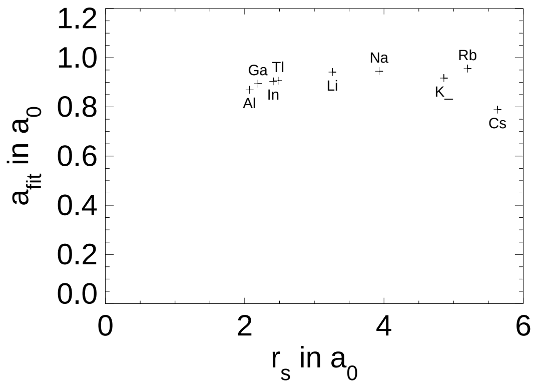
$\rightsquigarrow \quad \boxed{k_x = k_r \text{ and } \kappa_x = \kappa_r}$

Jellium Results: Fit of Selfconsistent Potentials

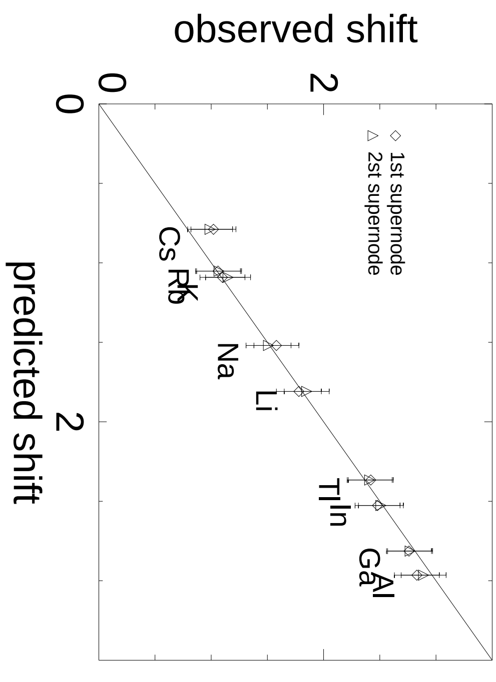
Fitpotential:

$$V(r, N) = \frac{-V_0}{1 + \exp((r - r_0 N^{1/3})/a)}$$

material	r_s	E_F	V_0	r_0	a	P	a/r_s
Al	2.07	−0.28	1.14	2.13	0.87	0.869	0.42
Ga	2.19	−0.28	1.04	2.26	0.89	0.855	0.41
In	2.41	−0.27	0.90	2.48	0.90	0.837	0.37
Tl	2.48	−0.27	0.87	2.56	0.92	0.831	0.37
Li	3.26	−0.24	0.59	3.34	0.94	0.770	0.29
Na	3.93	−0.22	0.46	4.04	0.95	0.722	0.24
K	4.86	−0.19	0.35	4.97	0.92	0.676	0.19
Rb	5.20	−0.18	0.32	5.32	0.96	0.661	0.18
Cs	5.63	−0.17	0.29	5.72	0.79	0.643	0.14



Supernodes: Compare linearized Semiclassics to Jellium Results



prediction:
$$N_{(1)}^{1/3} = 7.37 + \delta N_t(P_{semifit})\, a_{semifit}$$
$$N_{(2)}^{1/3} = 13.60 + \delta N_t(P_{semifit})\, a_{semifit}$$

predictions should get worse for lower densities, since Friedel-oscillations are neglected in semifit

Summary

- Jellium calculations for different densities
- Scaling analysis reveals *linear shift* of Supershells as function of electron density.
- *Improved convergence* of the periodic orbit expansion for $\tilde{E}$ allows description of Shells and Supershells in terms of only a few closed orbits.
- Semiclassics can be extended to realistic cluster potentials. *Linearization* holds in region of interest.
- Features of a cluster potential determinig the shell- and supershell structure are known. Allows sensible fit of selfconsistent potentials.
- Relevant *length scale* for Semiclassical arguments is the surface width a in units of r_s.
- Surface width a is nearly independent of r_s.
- Supershells in jellium calculations depend linearly on r_s.

Further plans:

- Introduce averaged Pseudopotentials.
- Introduce realistic ionic surface-profiles. Probably defines an additional length scale: atomic radius.