

# QMC Studies of Quantum Nanowires and Nanolayers

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# Quantum Nanowires and Nanolayers

- *Quantum nanowire* = 1D homogeneous electron gas.
- *Quantum nanolayer* = 2D homogeneous electron gas.
- QMC is the only accurate method for studying these systems.
- We have calculated some physically important quantities: binding energies and pair-correlation functions.<sup>1</sup>
- A more detailed QMC study of the 2D HEG is nearly complete: calculation of the zero-temperature phase diagram, PCF and momentum distribution.<sup>2</sup> (Using twist averaging, finite-size corrections and backflow.)
- A similar study has begun for the 1D HEG.

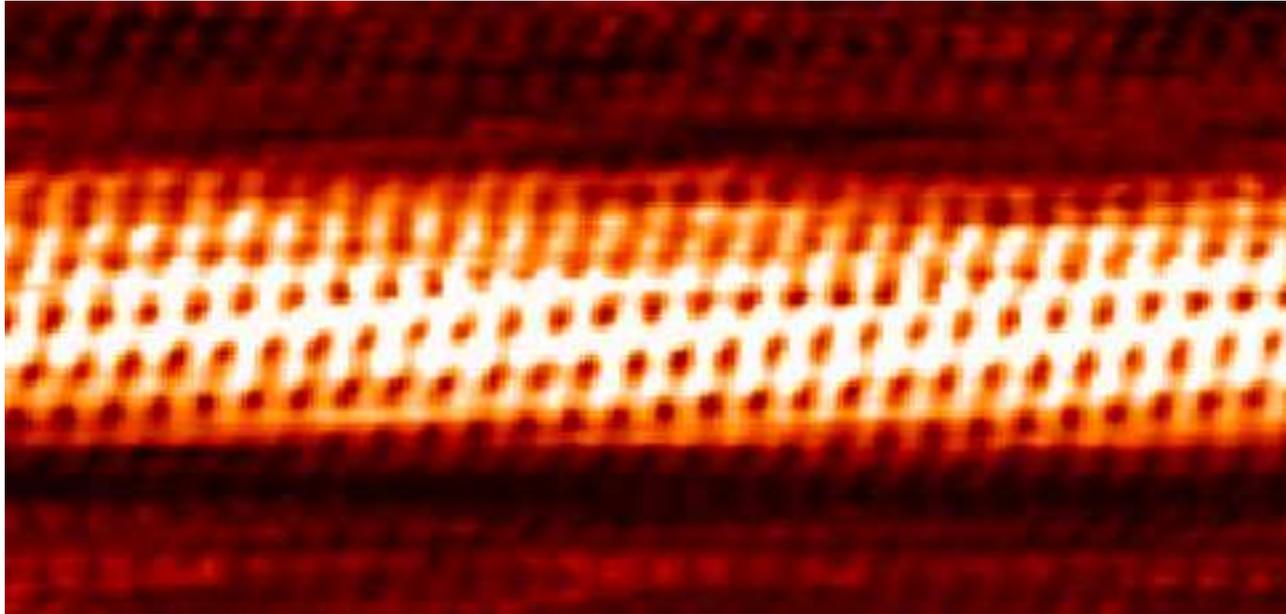
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<sup>1</sup>N. D. Drummond and R. J. Needs, Phys. Rev. Lett. **99**, 166401 (2007).

<sup>2</sup>N. D. Drummond and R. J. Needs, unpublished (2007).

## Quantum Nanowires (I)

- Experimental realisations of 1D HEGs: carbon nanotubes, Bechgaard salts, and one-dimensional channels etched on semiconductors.



*STM image of a carbon nanotube*

- Rich variety of strongly correlated electron physics to explore.

## Quantum Nanowires (II)

- 1D HEG forms a strongly correlated *Luttinger liquid*,<sup>3</sup> not a Fermi liquid.
- State of system immediately after the injection of an extra electron is orthogonal to the ground state (the *orthogonality catastrophe*).
- Carbon nanotubes are important components of proposed nanotechnological devices.
- Carbon nanotubes attract by *van der Waals* interactions, but the asymptotic behaviour assumed in current models of nanotechnological systems may be wrong.
- We have calculated the asymptotic form of the van der Waals attraction between thin 1D conducting wires using QMC.

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<sup>3</sup>J. M. Luttinger, J. Math. Phys. **4**, 1154 (1963); F. D. M. Haldane, J. Phys. C **14**, 2585 (1981).

# One-Dimensional Coulomb Interactions

- For a neutral 1D system the Fourier coefficients of the Coulomb interaction are

$$\tilde{v}_k = -\log(|k|^2/4) - 2\gamma,$$

where  $\gamma$  is Euler's constant.

- We use the method of Saunders *et al.*<sup>4</sup> to evaluate the 1D Coulomb interaction.
- Previous QMC studies<sup>5</sup> have used model interactions corresponding to a finite wire radius, thus avoiding the divergence at electron-electron coalescence points.
- For such interactions the Lieb-Mattis theorem (see later) implies that the ground state is paramagnetic.
- Our results correspond to the limit that the wire radius goes to 0: idealised limit.

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<sup>4</sup>V. R. Saunders *et al.*, *Comp. Phys. Comm.* **84**, 156 (1994).

<sup>5</sup>A. Malatesta and G. Senatore, *J. Phys. IV* **10**, 5 (2000); M. Casula *et al.*, *Phys. Rev. B* **74**, 245427 (2006).

## Nodal Surface and Magnetic Behaviour (I)

- Consider 2 distinguishable particles of charge  $q$  and  $Q$  and mass  $m$  and  $M$ , with relative position  $x$ . Hamiltonian:

$$\hat{H} = -\frac{1}{2\mu} \frac{d^2}{dx^2} + \frac{qQ}{|x|} + \hat{H}',$$

where  $\mu = mM/(m + M)$  is the reduced mass and  $\hat{H}'$  does not depend on  $x$ .

- Suppose wave function is  $\Psi = a_0 + \mathcal{O}(x)$ .
- Suppose  $a_0 \neq 0$ . Then local energy

$$E_L = \frac{\hat{H}\Psi}{\Psi} = \frac{qQ}{|x|} + \mathcal{O}(x^0).$$

This contains a nonintegrable divergence, so the energy expectation is undefined. Hence must have  $a_0 = 0$ . So  $\Psi = 0$  at **all** coalescence points.

## Nodal Surface and Magnetic Behaviour (II)

- Hence the nodal surface is the set of points at which particles coincide.
- The nodal surface, and hence the fixed-node DMC energy, is independent of the spin polarisation.
- The 1D GS nodal surface is exact, so the DMC energies of 1D HEGs are exact.
- Therefore the GS energy of the 1D HEG is independent of the spin polarisation.
- Odd behaviour: if the charges are 0 then the ferromagnetic HEG is higher in energy than the paramagnetic HEG, but as soon as the charge is nonzero, paramagnetic and ferromagnetic energies are degenerate.
- Easiest way of getting nodal surface right: just work with ferromagnetic 1D HEGs.

## Nodal Surface and Magnetic Behaviour (III)

- Lieb–Mattis theorem<sup>6</sup>: consider a 1D Hamiltonian with a real, symmetric, *nonpathological* potential. If total spin  $S' < S$  then GS energies satisfy  $E_0(S') < E_0(S)$ .
- However, 1D Coulomb interaction is pathological in the formal sense used by L&M: wave function is zero at points other than same-spin coalescence points (namely opposite-spin coalescence points).
- Weaker form of L–M holds if the potential is pathological: if  $S' < S$  then  $E_0(S') \leq E_0(S)$ . So our conclusion that paramagnetic and ferromagnetic states are degenerate in energy does not contradict the L–M theorem.
- In real 1D systems the wire radius is finite, so that the electron–electron interaction is nonpathological. Hence real 1D systems will be paramagnetic by the L–M theorem.

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<sup>6</sup>E. Lieb and D. Mattis, Phys. Rev. **125**, 164 (1962).

## Hartree–Fock Theory for 1D HEG (I)

Hartree–Fock kinetic energy ( $T$ ) and exchange ( $X$ ) energies of 1D HEG:

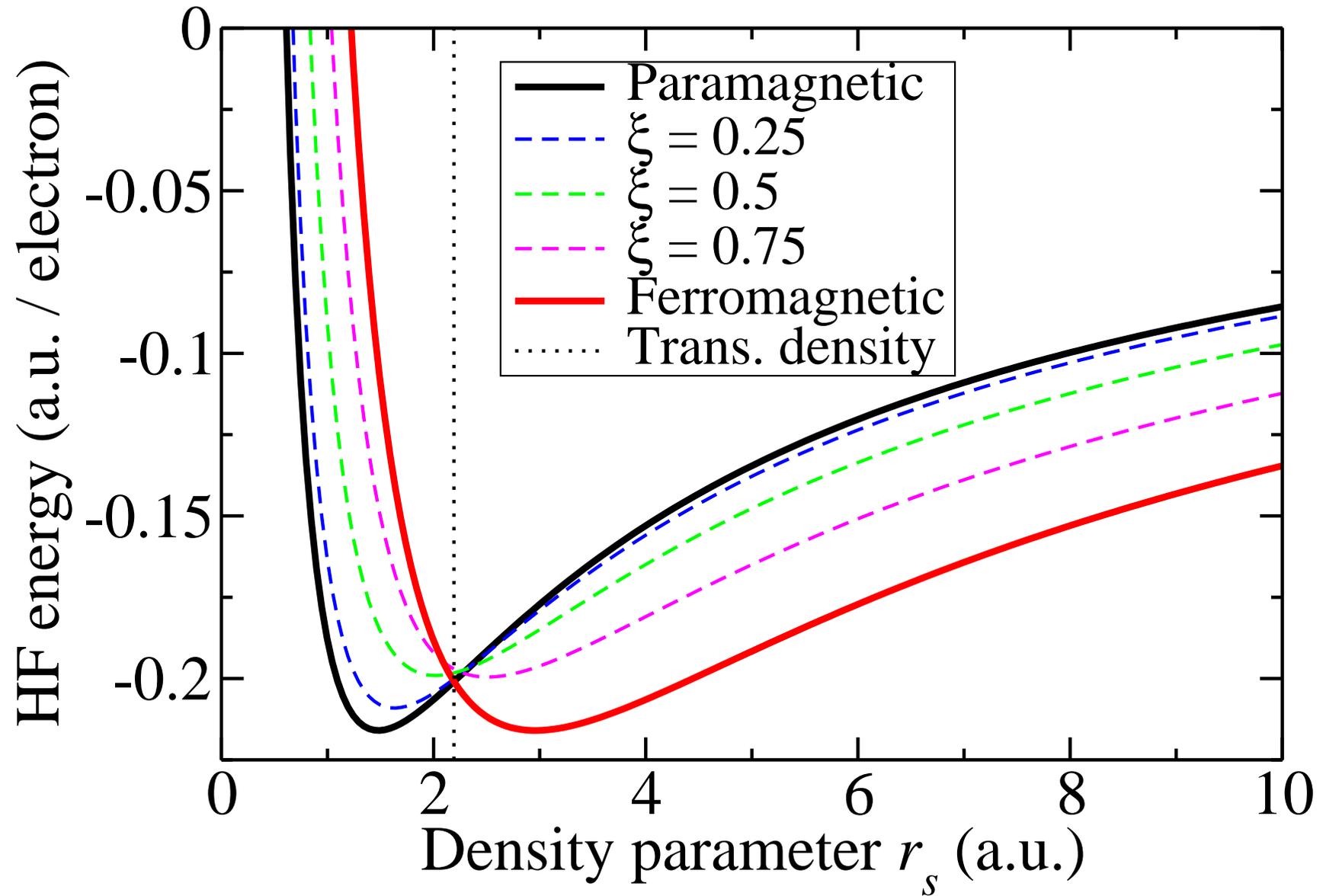
$$T = \frac{\pi^2}{192r_s^2} [(1 + \xi)^3 + (1 - \xi)^3]$$

$$X = \frac{1}{8r_s} \left\{ (1 + \xi)^2 \left( \log \left[ \frac{\pi(1 + \xi)}{4r_s} \right] + \gamma - \frac{3}{2} \right) + (1 - \xi)^2 \left( \log \left[ \frac{\pi(1 - \xi)}{4r_s} \right] + \gamma - \frac{3}{2} \right) \right\}$$

where  $\xi$  is the spin polarisation and  $\gamma$  is Euler's constant.

Hartree–Fock theory predicts a sharp transition from a paramagnetic fluid to a ferromagnetic one at  $r_s = 2.19$  a.u.

## Hartree-Fock Theory for 1D HEG (II)



# Wire / Biwire QMC Calculations (I)

- We use a ferromagnetic Slater wave function with plane-wave orbitals.
- **Jastrow factor**: two-body terms ( $u + p$ ) satisfying Kato cusp conditions.
- **Backflow function**: two-body term ( $\eta$ ) makes a significant improvement, even though the (already exact) nodal surface is not altered.
- Results for 15-electron wire at  $r_s = 3$  a.u.:

Method	Energy (a.u. per el.)	Variance (a.u.)	Percentage corr. energy
HF	-0.215943040112	—	0%
SJ-VMC	-0.2319668(4)	0.0000360(2)	99.974(3)%
SJB-VMC	-0.2319710(3)	0.0000046(1)	100.000(3)%
SJB-DMC	-0.2319709(3)	—	100%

## Wire / Biwire QMC Calculations (II)

- DMC energy suffers from very little time-step and population-control bias, because nodes are exact and trial wave function is so accurate.
- Use time steps of 0.04 a.u., 0.2 a.u. and 2.5 a.u. in our calculations at  $r_s = 1, 3$  and 10 a.u., respectively and populations of 2048 configurations.
- Verified that energies do not change significantly when time step is halved; no need to extrapolate to zero time step.

## Binding Energy of a Biwire (I)

- Consider 2 parallel conducting nanowires (i.e. 1D HEGs, each with a neutralising line of background charge) with finite separation  $z$ .
- They are attracted to each other by van der Waals forces.
- Standard theory: van der Waals energy between wire elements  $\delta l_1$  and  $\delta l_2$  separated by  $r$  is  $\alpha\delta l_1\delta l_2/r^6$  where  $\alpha$  is a constant.
- Current models of interacting carbon nanotubes etc. often use Lennard–Jones potentials [ $U(r) = -A/r^6 + B/r^{12}$ ] to capture this long-range behaviour.<sup>7</sup>
- At wide separation the binding energy per particle is

$$U(z) = r_s \int_{-\infty}^{\infty} \frac{\alpha}{(x^2 + z^2)^3} dx \sim z^{-5}.$$

- Clearly appropriate for an insulator. What about a conductor?

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<sup>7</sup>See L. A. Girifalco *et al.*, Phys. Rev. B **62**, 13104 (2000) and references thereto.

## Binding Energy of a Biwire (II)

- Recently-calculated binding energy per electron in the random phase approximation<sup>8</sup>:

$$U(z) \approx -\frac{\sqrt{r_s}}{16\pi z^2 [\log(2.39z/b)]^{3/2}}.$$

where  $b$  is the (finite) wire radius.

- RPA is believed to give the correct asymptotic form of binding energy, although the prefactor is approximate.
- Mean free path in carbon nanotubes can be  $\sim 1 \mu\text{m}$ , much greater than the range of  $z$  we study: impurities are not a problem.
- RPA may be invalid at low densities, where correlation effects become significant.

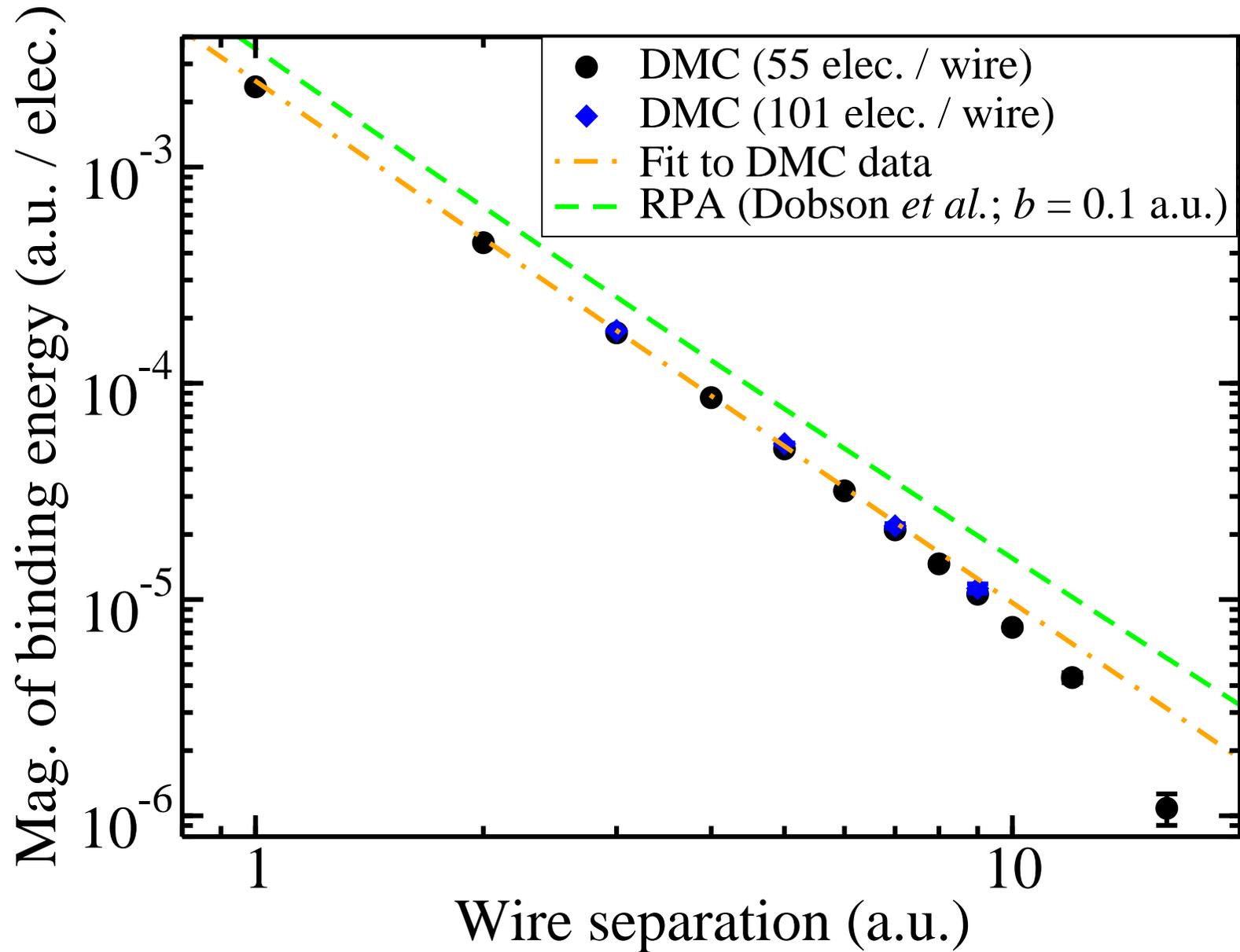
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<sup>8</sup>J. F. Dobson *et al.*, Phys. Rev. Lett. **96**, 073201 (2006).

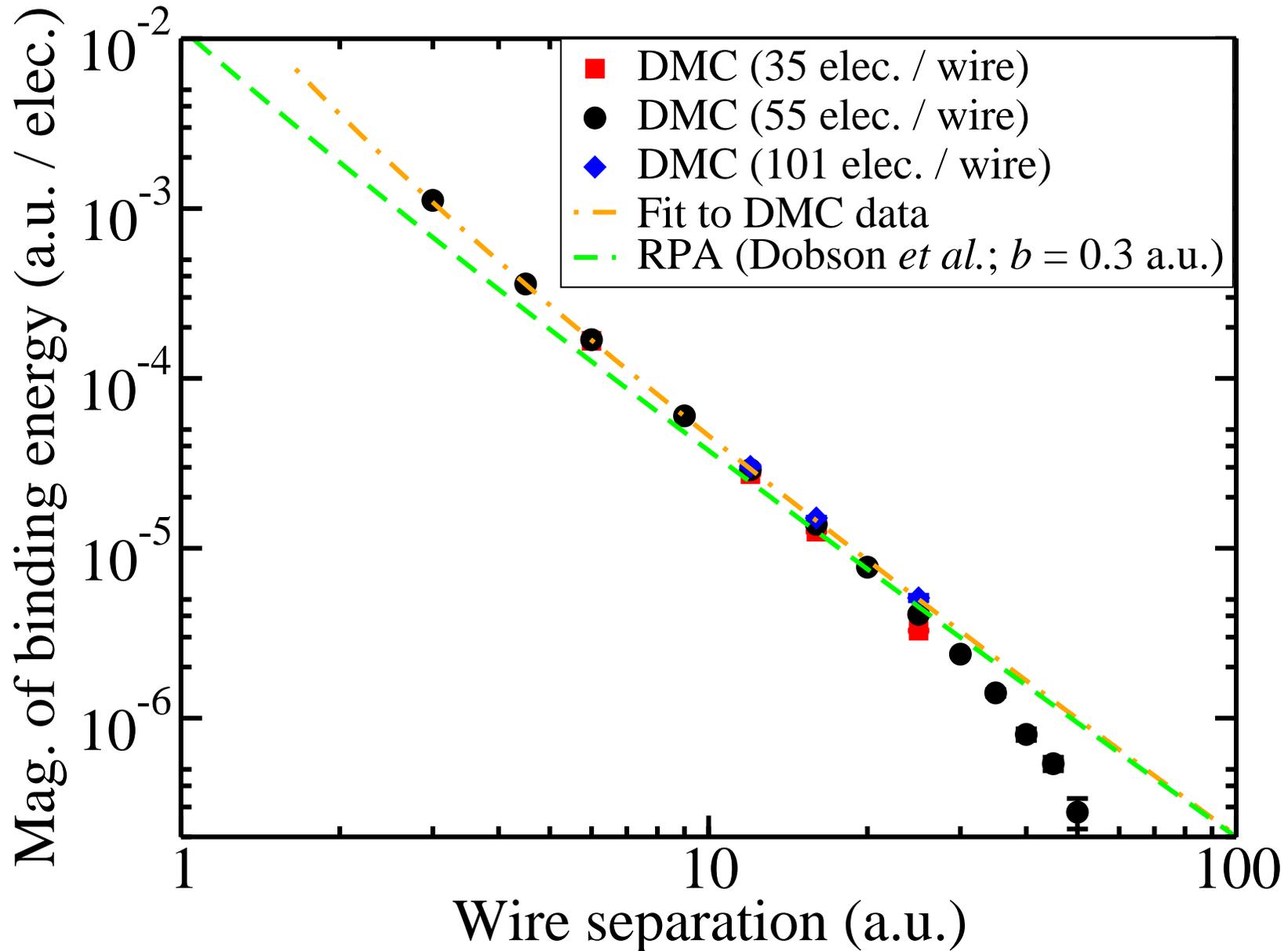
## Binding Energy of a Biwire (III)

- Each wire has a neutralising background; need to add interaction between (a) electrons in wire 1 and background 2, (b) electrons in wire 2 and background 1 and (c) interaction between backgrounds 1 and 2.
- (a), (b) and (c) have same magnitude, but (c) has opposite sign. So, must subtract off electrostatic energy of a pair of parallel lines of the same charge. Hence must add  $E_{\text{cap}} = \log(z)/(2r_s)$  to our QMC energies.
- Perform biwire and monowire calculations with the same number of electrons per wire; finite-size errors should cancel. No need to twist average or add finite-size corrections.
- Expect results to be valid so long as separation is less than the simulation-cell size; after that system resembles a pair of insulating wires. Fit QMC data in range  $r_s \ll z \ll Nr_s$ .

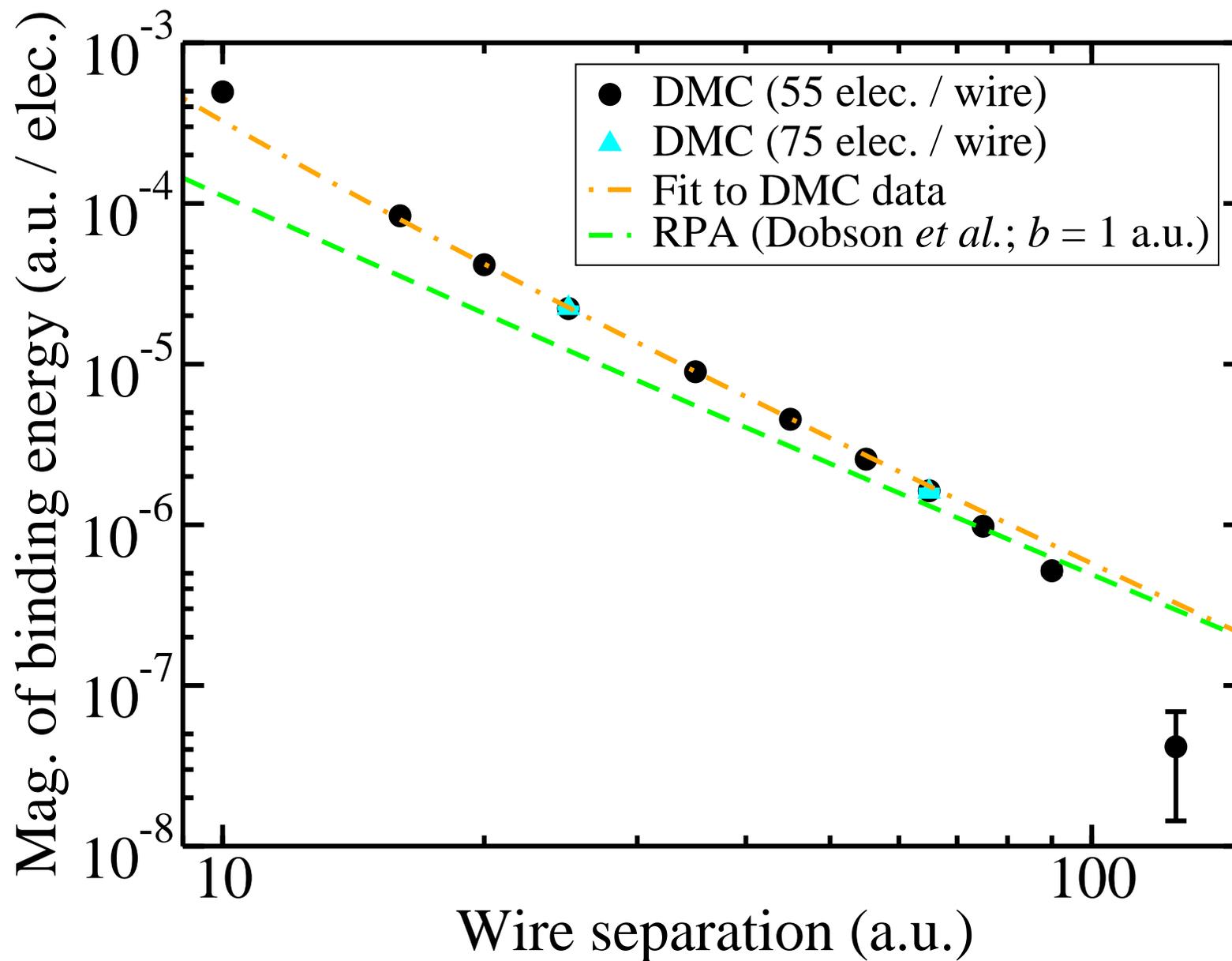
## Binding Energy of a Biwire (IV): $r_s = 1$ a.u.



## Binding Energy of a Biwire (IV): $r_s = 3$ a.u.



## Binding Energy of a Biwire (IV): $r_s = 10$ a.u.

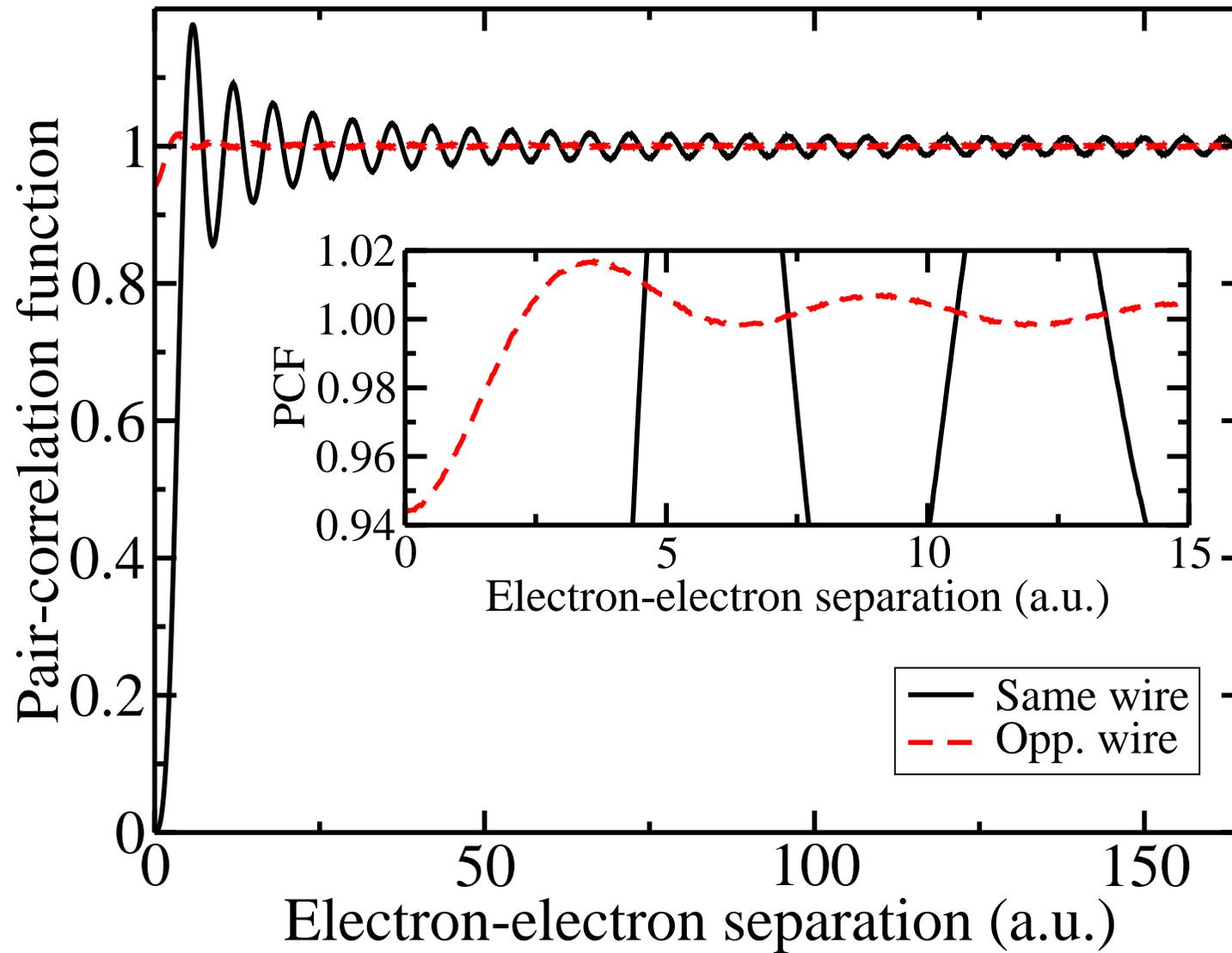


## Binding Energy of a Biwire (V)

$r_s$ (a.u.)	Asymptotic binding energy (a.u. per electron)	
	RPA	DMC
1	$-0.0199z^{-2} [\log(2.39z/b)]^{-3/2}$	$-0.0815z^{-2.28} [\log(27000z)]^{-3/2}$
3	$-0.0345z^{-2} [\log(2.39z/b)]^{-3/2}$	$-0.0225z^{-1.98} [\log(1.950z)]^{-3/2}$
10	$-0.0629z^{-2} [\log(2.39z/b)]^{-3/2}$	$-0.0967z^{-2.17} [\log(0.492z)]^{-3/2}$

- The DMC binding energies are in broad agreement with the RPA predictions. They fall off much less rapidly than the  $z^{-5}$  decay predicted by the standard theory.
- It is not meaningful to compare the prefactors because the RPA expression is not valid in the limit that  $b \rightarrow 0$ .
- Uncertainties in exponents are about 0.1–0.2.

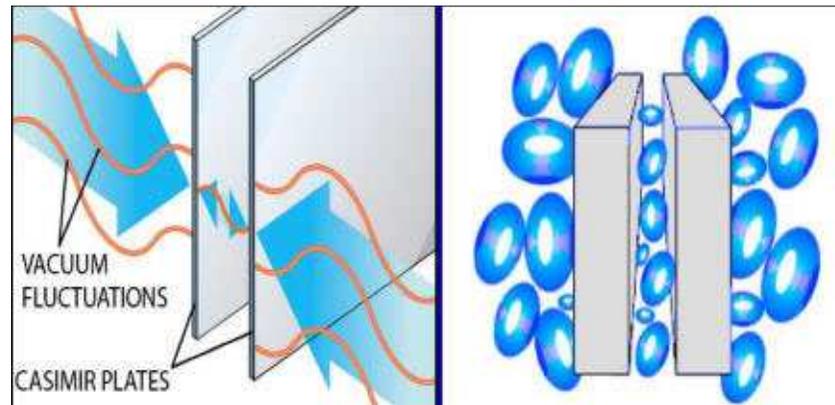
## Biwire Pair-Correlation Functions



Biwire,  $r_s = 3$  a.u.,  $z = 3$  a.u.

## Casimir Effect and van der Waals Binding

- At very large separations ( $z > 70246r_s^2$  within the RPA) the **Casimir effect** is the dominant source of attraction between thin, neutral metallic layers.<sup>9</sup>



- The zero-point energy of photon modes between the layers depends on the separation; this results in an attractive force between the layers. Use QED to calculate.
- **Casimir binding energy:**  $E_{\text{cas}} = -c\pi^2/(720z^3)$ , where  $c$  is the speed of light.
- We will only consider the regime in which **van der Waals** forces dominate, i.e. the regime described by the nonrelativistic many-electron Schrödinger equation.

<sup>9</sup>H. B. G. Casimir and D. Polder, Phys. Rev. **73**, 360 (1948); B. E. Sernelius and P. Björk, Phys. Rev. B **57**, 6592 (1998).

## Binding Energy of a Thin Metallic Bilayer (I)

- Standard theory: interaction between surface elements of area  $\delta a_1$  and  $\delta a_2$  separated by  $r$  is  $\alpha\delta a_1\delta a_2/r^6$ , where  $\alpha$  is a constant; so binding energy per particle is

$$U(z) = \frac{\pi r_s^2}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{\alpha}{(x^2 + y^2 + z^2)^3} dx dy \sim z^{-4}.$$

- Is inevitable consequence of using Lennard-Jones potentials for bilayer.
- Clearly appropriate for an insulator. What about a conductor?
- RPA binding energy of a HEG bilayer is<sup>10</sup>

$$U(z) = \frac{-0.012562\sqrt{\pi}r_s}{2z^{5/2}}.$$

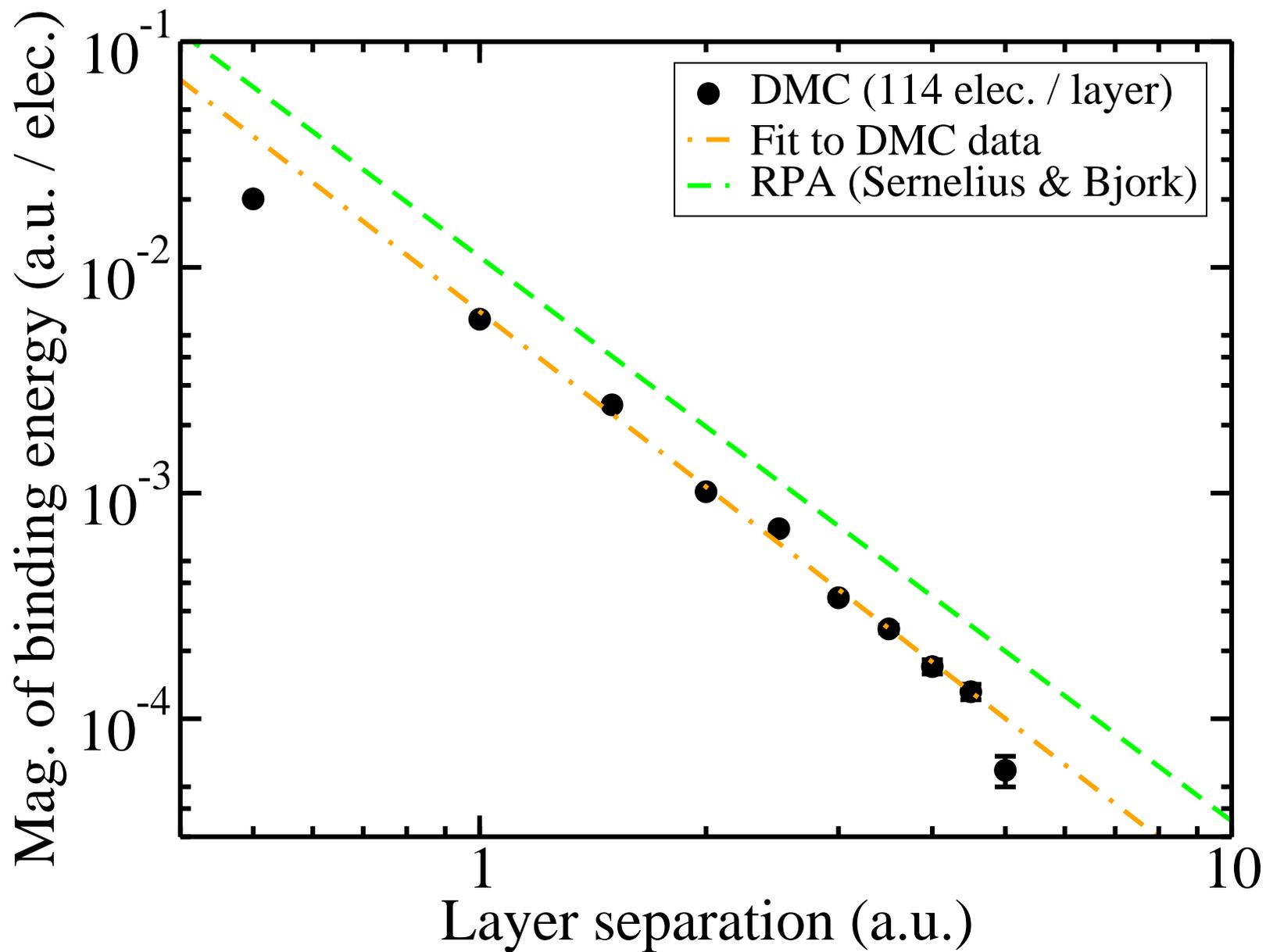
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<sup>10</sup>B. E. Sernelius and P. Björk, Phys. Rev. B **57**, 6592 (1998).

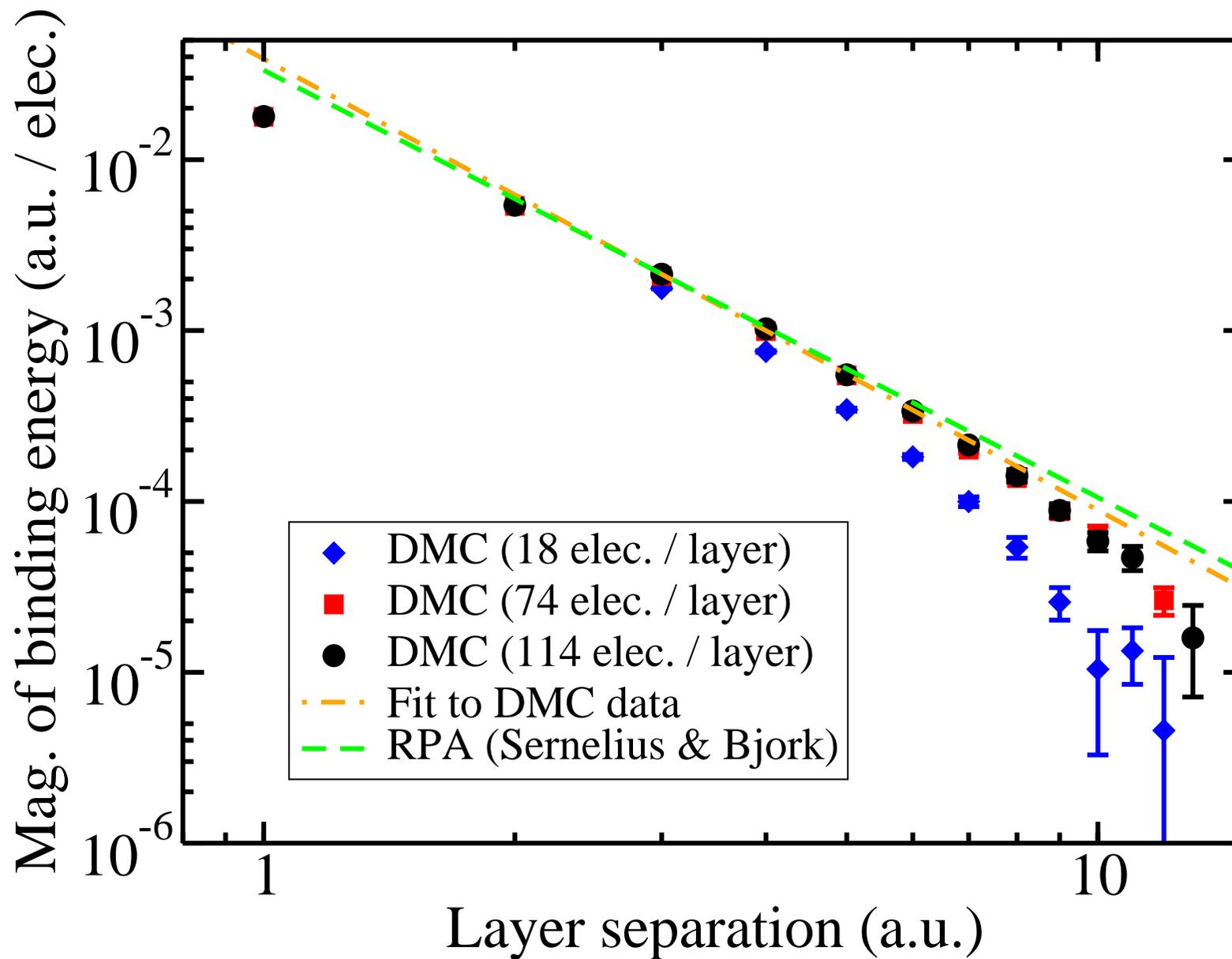
## Binding Energy of a Thin Metallic Bilayer (II)

- As with biwire, perform DMC calculations (i) to verify asymptotic form predicted by RPA and (ii) to obtain the correct prefactor.
- “Capacitor energy” ( $E_{\text{cap}} = z/r_s^2$ ) must be added to our DMC energies.
- Expect large cancellation of finite-size effects when monolayer energy is subtracted from bilayer energy, so long as separation is less than simulation-cell length.
- Used Slater-Jastrow-backflow wave function at  $r_s = 1$  a.u.; Slater-Jastrow wave function at other densities.
- Used time steps of 0.02 a.u., 0.05 a.u. and 0.5 a.u. and populations of 1024, 320 and 1024 configurations in our calculations at  $r_s = 1, 3$  and 10 a.u., respectively.
- Verified that time-step bias is negligible at  $r_s = 1$  and 3 a.u. by halving time step.

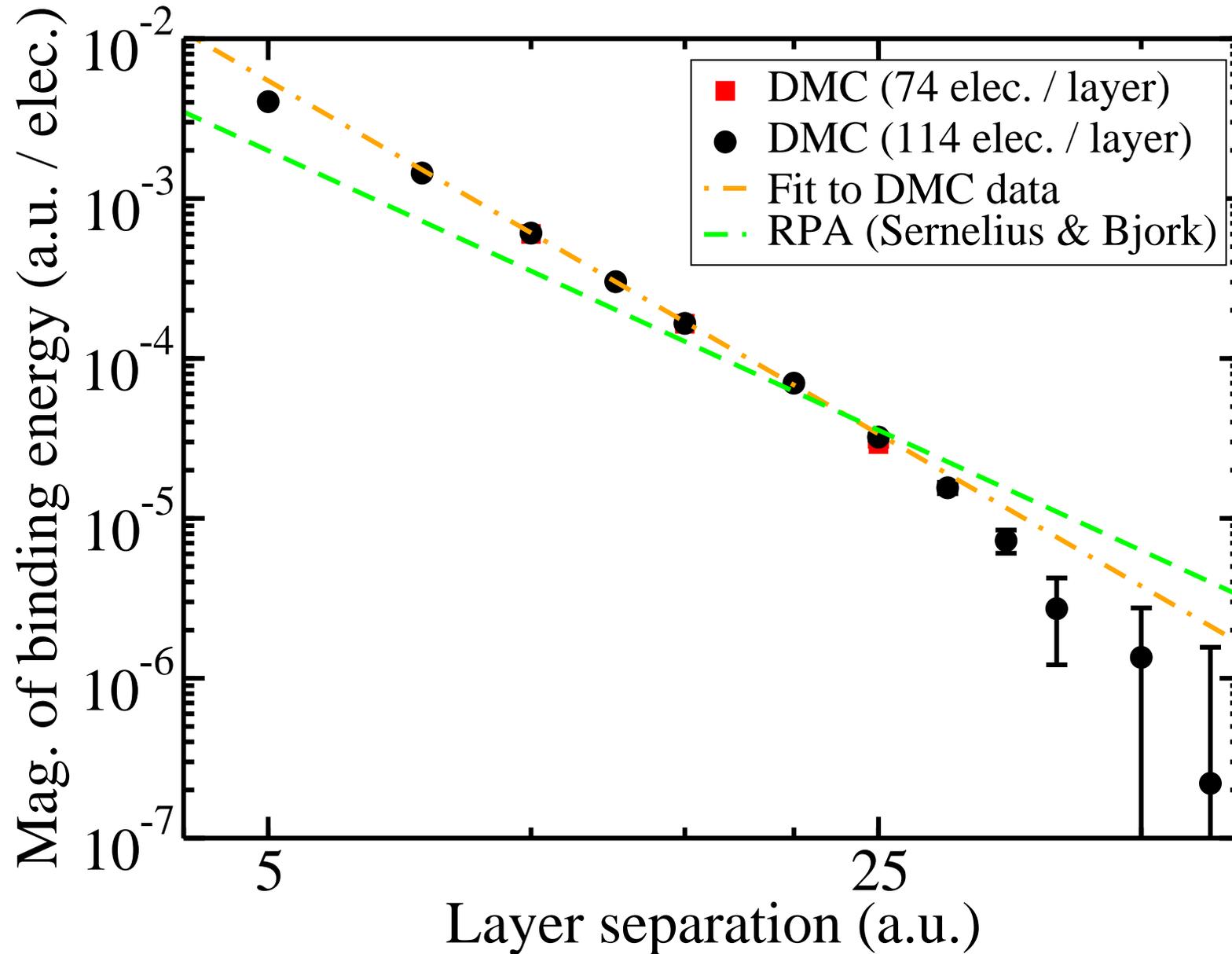
## Binding Energy of a Metallic Bilayer (III): $r_s = 1$ a.u.



## Binding Energy of a Metallic Bilayer (III): $r_s = 3$ a.u.



## Binding Energy of a Metallic Bilayer (III): $r_s = 10$ a.u.

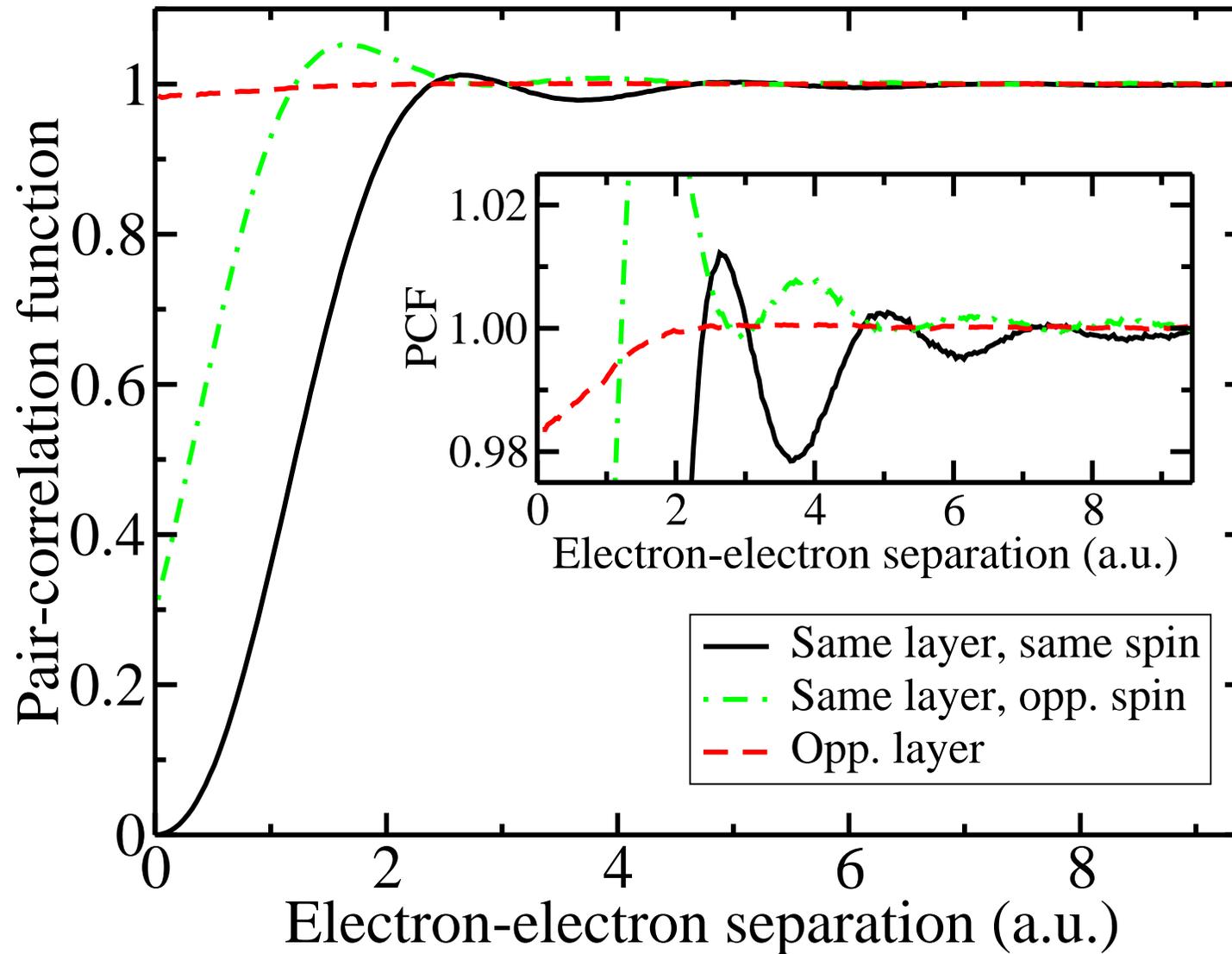


## Binding Energy of a Metallic Bilayer (IV)

$r_s$ (a.u.)	Asymptotic binding energy (a.u. per electron)	
	RPA	DMC
1	$-0.011133z^{-5/2}$	$-0.00637z^{-2.58}$
3	$-0.033398z^{-5/2}$	$-0.03880z^{-2.64}$
10	$-0.111330z^{-5/2}$	$-0.88200z^{-3.16}$

- The DMC binding energies are in broad agreement with the RPA predictions. They fall off much less rapidly than the  $z^{-4}$  decay predicted by the standard theory.
- Uncertainties in exponents are about 0.1–0.2.
- $r_s = 1$  a.u.: RPA gives correct behaviour but somewhat overestimates the prefactor.
- $r_s = 3$  a.u.: the DMC and RPA results are in good agreement.
- $r_s = 10$  a.u.: the DMC binding energy falls off slightly more rapidly than the RPA binding energy. Perhaps the RPA is missing some important correlation effects at low density.

## Bilayer Pair-Correlation Functions



Bilayer,  $r_s = 1$  a.u.,  $z = 2$  a.u., SJB wave function, extrapolated PCF

# Conclusions

- We have obtained accurate binding energies for pairs of thin, parallel, metallic layers and wires using DMC.
- Our results are in broad agreement with recent RPA calculations of the binding energy. *This confirms that the common practice of using Lennard-Jones pair potentials to describe the binding of metallic wires and layers is qualitatively incorrect.*
- Our data could be used to parametrise the wire–wire and layer–layer interaction potentials used in models of nanotechnological devices, or to help in the construction of van der Waals energy functionals for use in DFT calculations.
- Some differences between DMC and RPA: at low densities the DMC bilayer binding energy falls off slightly more rapidly.

# Acknowledgements

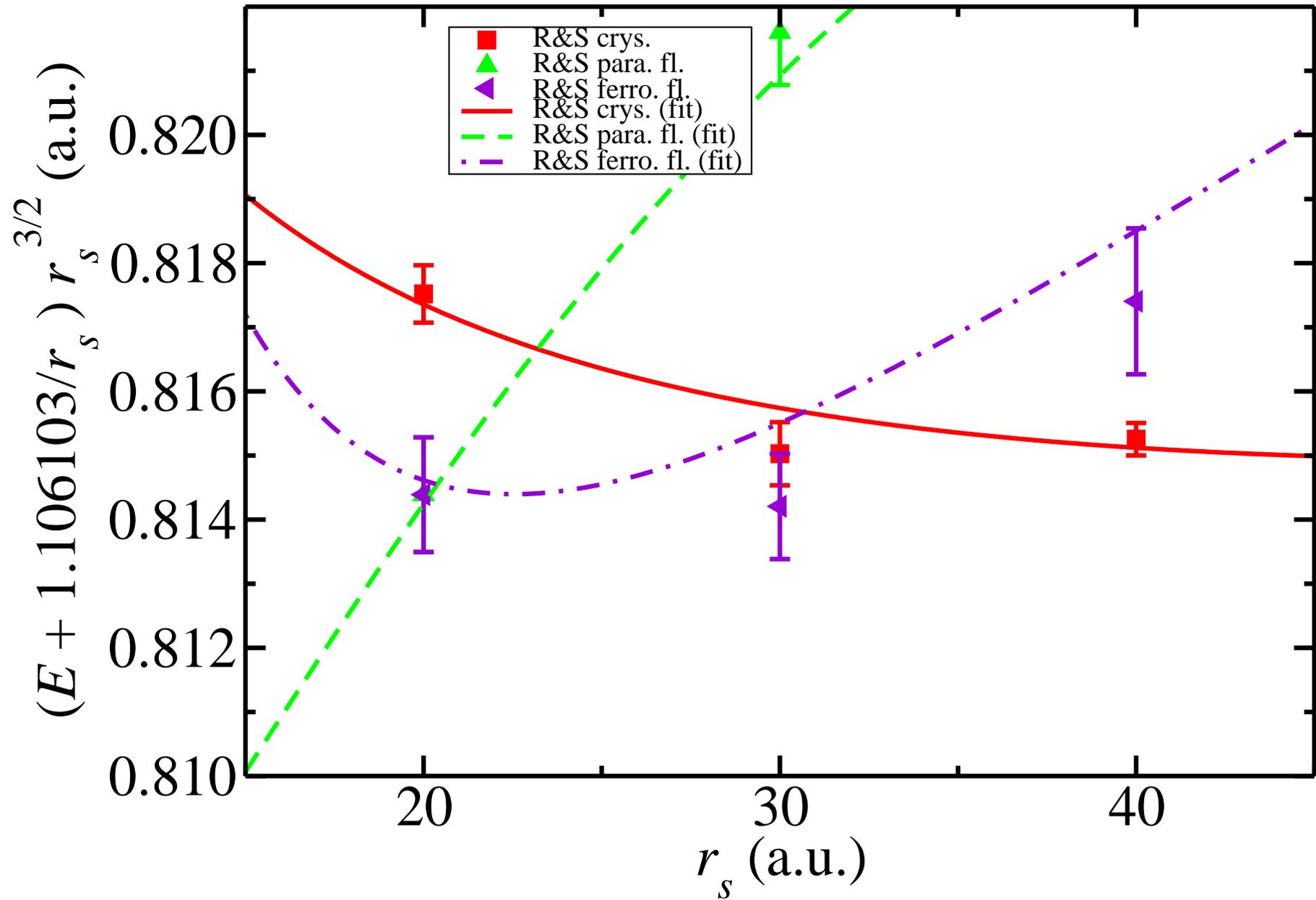
We acknowledge financial support from Jesus College, Cambridge and the Engineering and Physical Sciences Research Council.



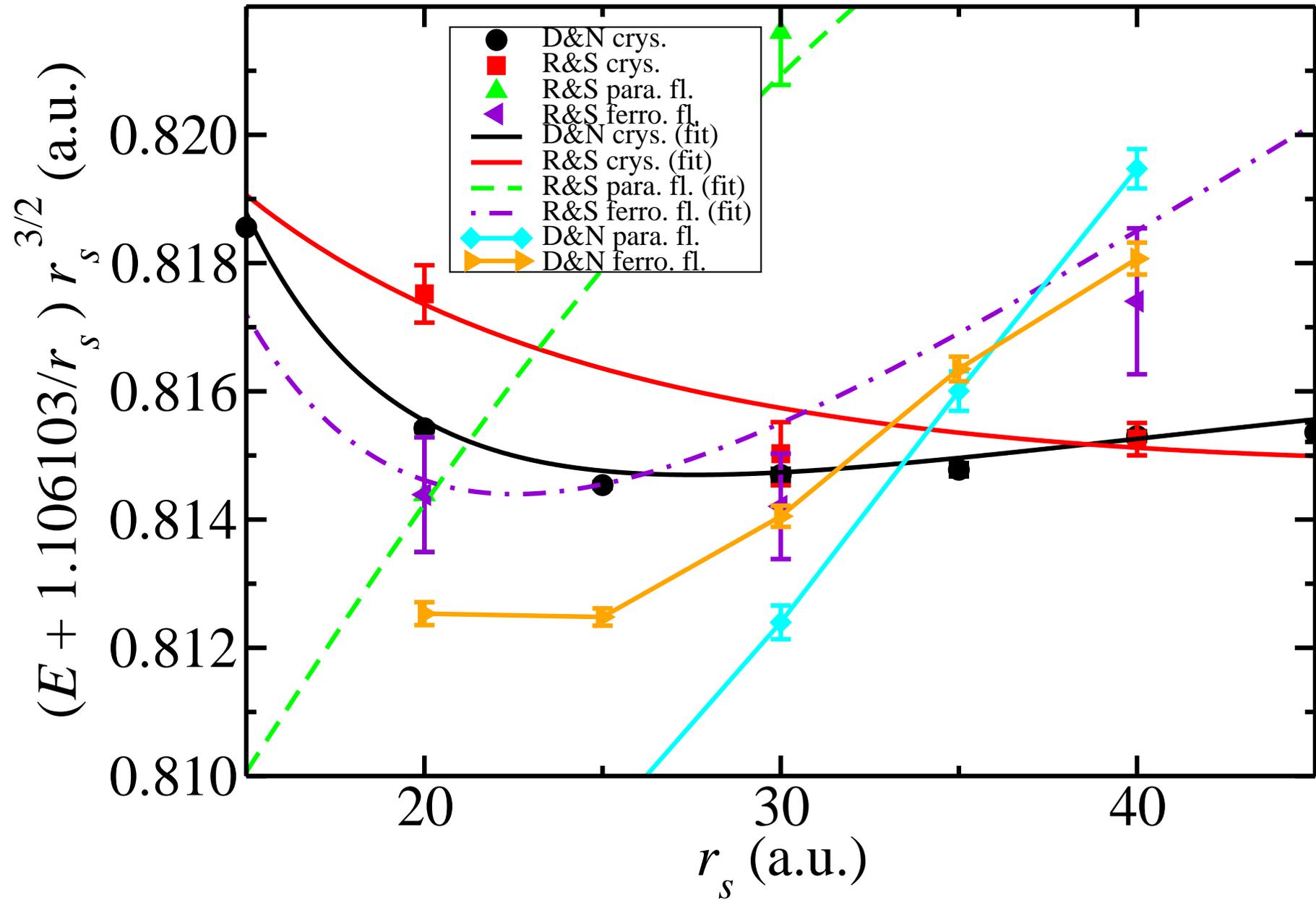
Computing resources were provided by the Cambridge High Performance Computing Service.



## 2D HEG Energy Diagram (I)



## 2D HEG Energy Diagram (I)



## 2D HEG Energy Diagram (II)

- Ferromagnetic fluid is never stable.
- Wigner crystallisation occurs at  $r_s = 33 \pm 2$  a.u.
- Work in progress; these are preliminary results.