First-Principles Study of a Positron Immersed in an Electron Gas

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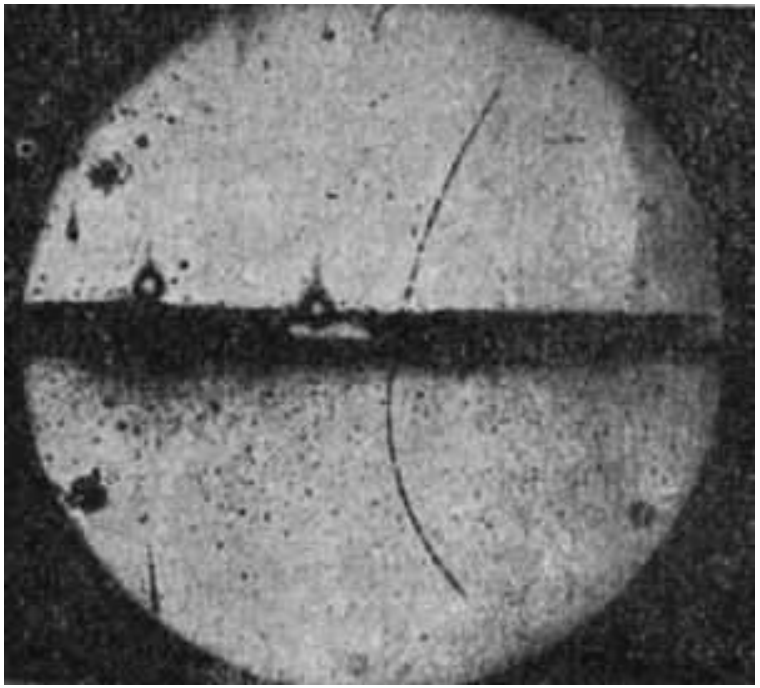
Positrons and Positronium Atoms

Positrons are **anti-electrons** (solutions of Dirac equation).



Positrons are produced in β^+ decays of proton-rich nuclei,
e.g. ${}^{25}_{13}\mathrm{Al}_{12} \to {}^{25}_{12}\mathrm{Mg}_{13} + \beta^+ + \nu$.

A positron may bind with an electron to form a *positronium atom*.

Ground-state energy of positronium is $-1/4$ a.u. (Like a hydrogen atom, but the reduced mass is $1/2$ a.u.)

Positron Annihilation

Annihilation of a parallel-spin electron–positron pair is a third-order process in quantum electrodynamics, producing three photons.

Annihilation of an antiparallel-spin electron–positron pair is a second-order process, producing two 0.511 MeV photons.

We consider only two-photon annihilation events because they are (a) much more frequent and (b) much more useful.

Two-photon annihilation cross-section is $\sigma_{2\gamma} = \pi/(vc^3)$, where v is the positron velocity and c is the speed of light.[1]

Positron annihilation is widely used to study material properties.

Usual source of positrons in experiments: ${}^{22}_{11}\mathrm{Na}_{11} \rightarrow {}^{22}_{10}\mathrm{Ne}_{12} + \beta^+ + \nu + \gamma$.

Energy of photon emitted at birth of positron: 1.274 MeV.

[1] P. A. M. Dirac, Proc. Cam. Phil. Soc. **26**, 361 (1930).

Positron Lifetime Spectroscopy (I)

Suppose a positron is injected into a sample of material.

Positron rapidly thermalises and diffuses through material, before ending up in its ground state. (Often settles in **negatively charged defects**.)

Positron remains in ground state for some time before annihilating an electron.

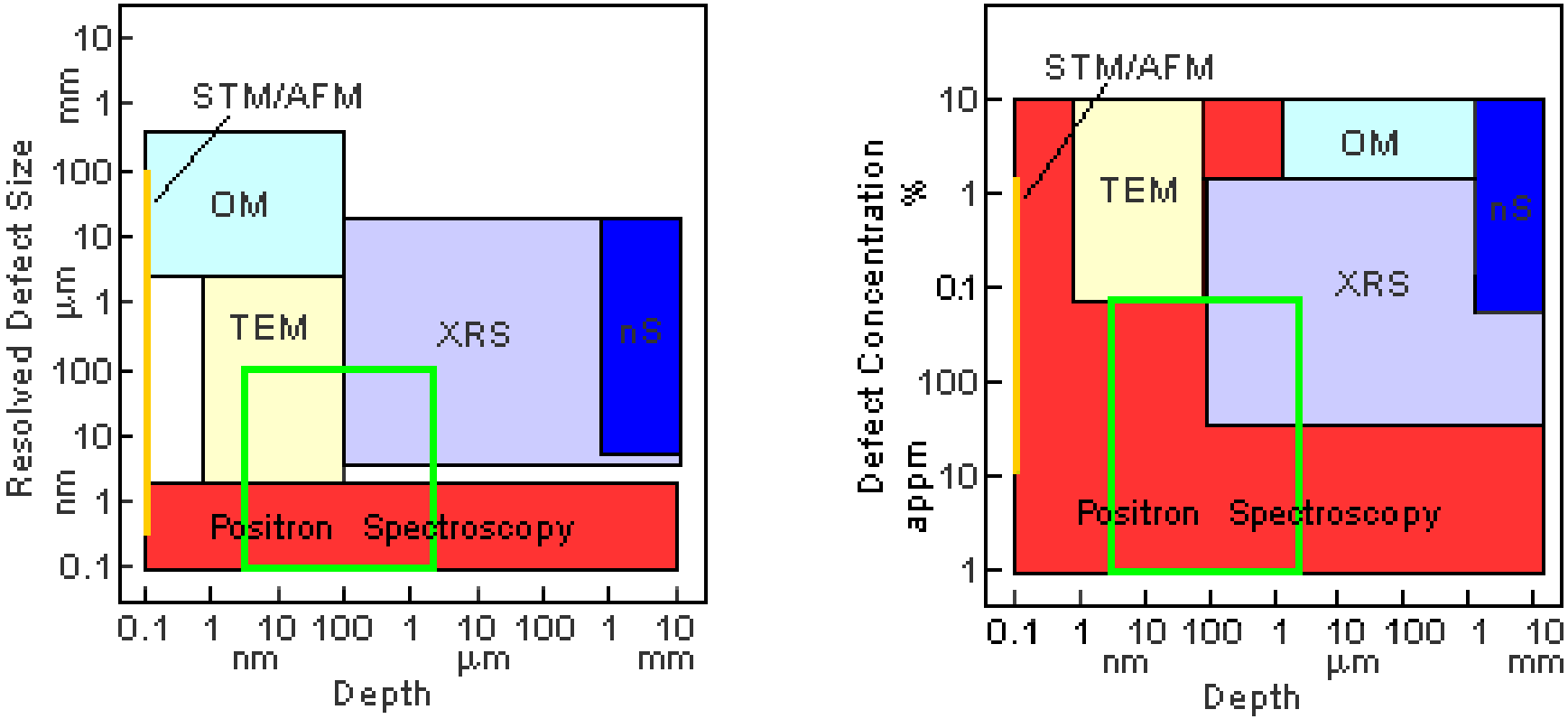
POLIS: measure time difference between positron birth (one 1.274 MeV photon emitted) and annihilation (two 0.511 MeV photons emitted).

Annihilation rate is characteristic of the defects at which positrons settle.

Sensitive, nondestructive technique allowing simultaneous measurement of type and quantity of defects in metals and semiconductors.[2]

[2] R. Krause-Rehberg and H. S. Leipner, *Positron Annihilation in Semiconductors*, Springer–Verlag (1999).

Positron Lifetime Spectroscopy (II)



Sensitivity of different experimental methods to defect concentration and size as a function of depth. Green box indicates depth, size and concentration relevant to studies of defects in electronic interconnects on semiconductor chips.

Annihilating-Pair Momentum Spectroscopies (I)

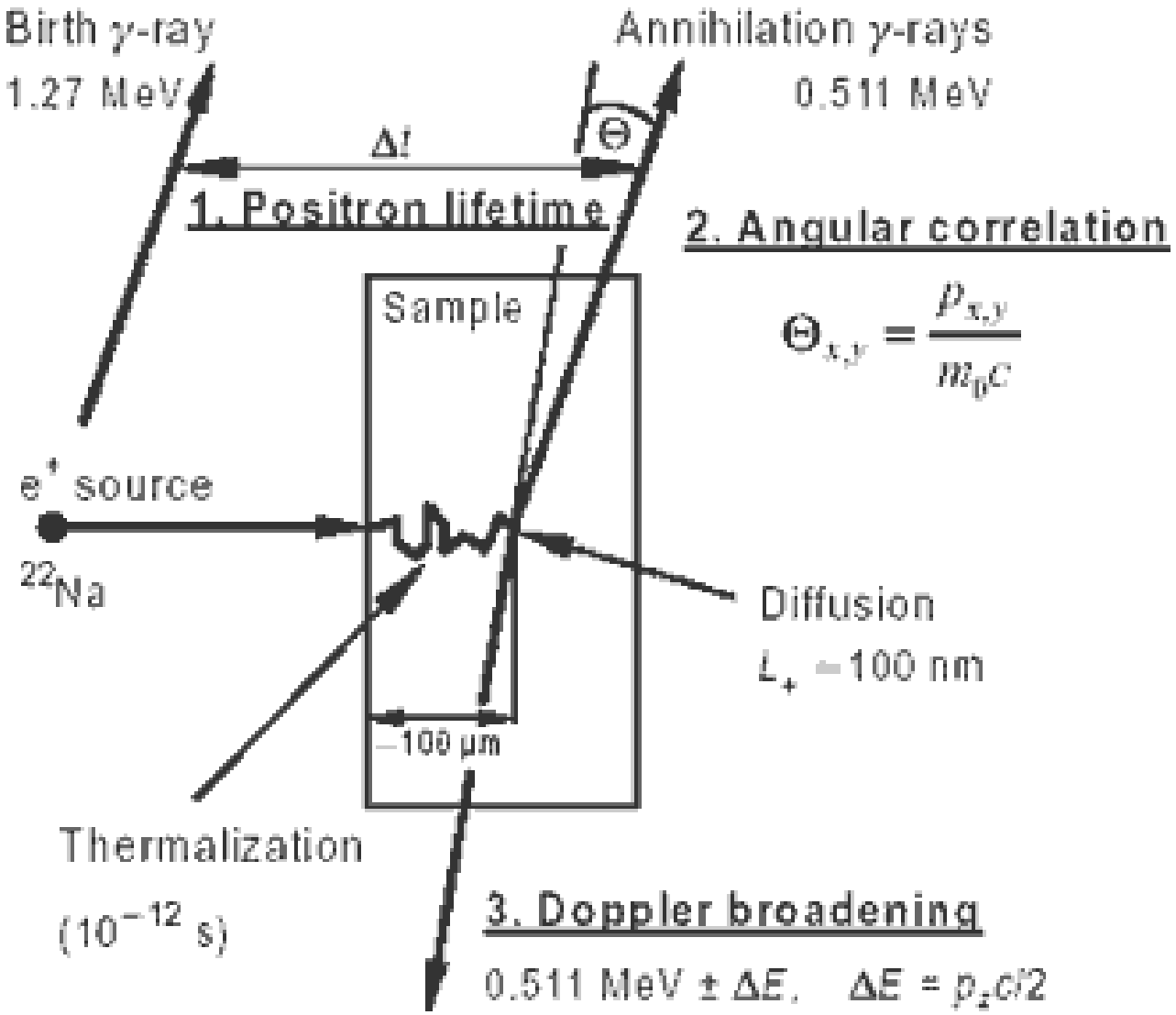
Conservation of momentum: total momentum of annihilation γ-rays is equal to the momentum of the **annihilating electron–positron pair**.

In a single-particle theory, the ground-state of the positron has zero momentum, so the momentum of the annihilation radiation is just the momentum of the electron.

Measure distribution of momenta of annihilation radiation to find out about distribution of electron momenta at defect at which positron settles.

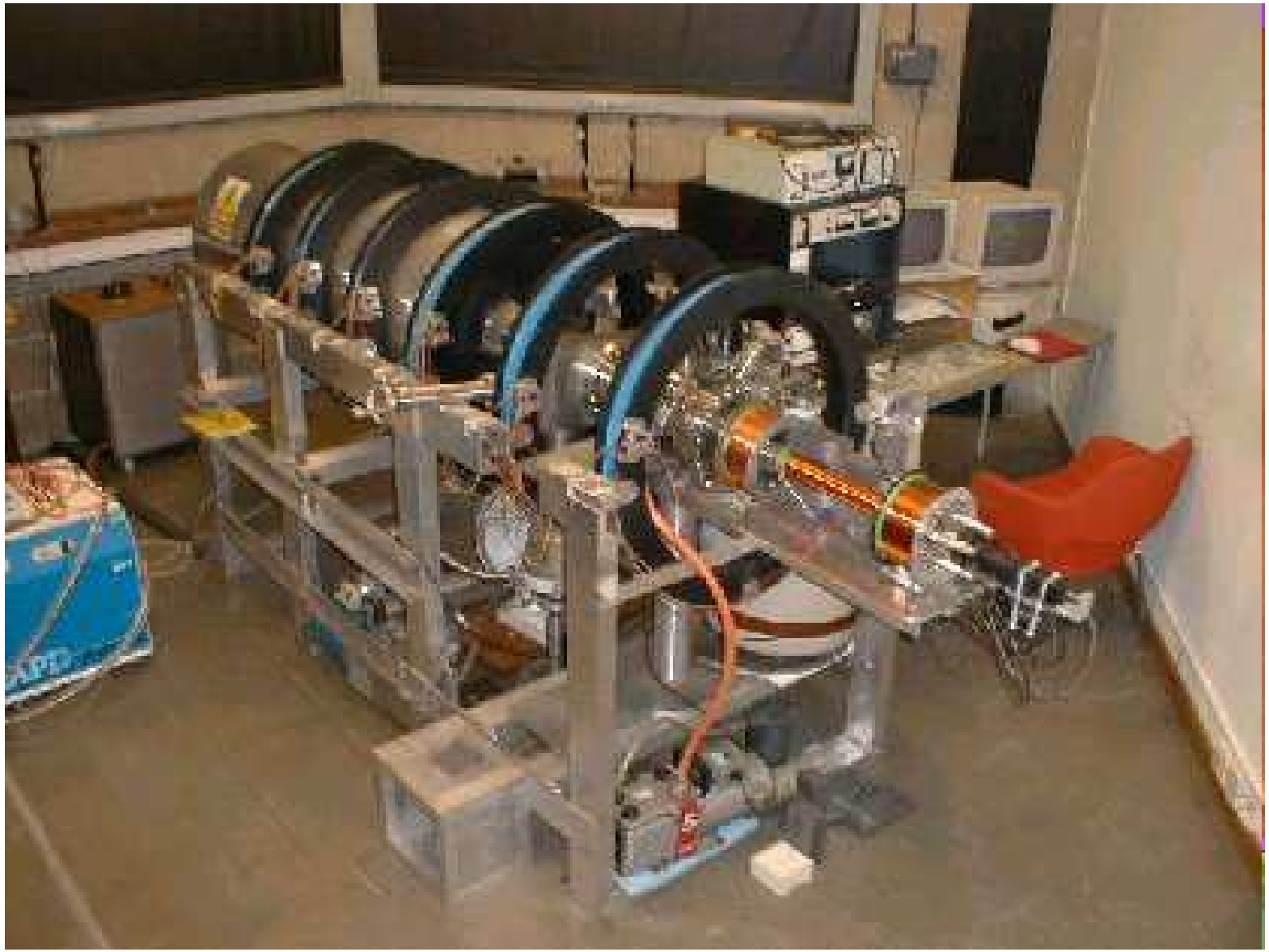
Angular correlation of annihilation radiation (ACAR) spectroscopy and *Doppler-broadening spectroscopy* (DOBS) are powerful methods for identifying defects and measuring Fermi surfaces.

Annihilating-Pair Momentum Spectroscopies (II)



POLIS, DOBS and ACAR spectroscopy.

Annihilating-Pair Momentum Spectroscopies (III)



Magnetically confined positron beam for DOBS experiments at the University of Bath

Applications of Positron Annihilation Spectroscopy

Recent PAS studies at the University of Bath include[3]:

- *Surface modification of polymer films by laser or plasma treatment*;
- *Defects caused by the implantation of* Ge *ions into* SiC;
- *Transition region between* SiO_2 *and* Si;
- *Fluorine diffusion and agglomeration in* Si;
- *Interfaces between nanocrystals of* Si *and a silica matrix*;
- *Defects in ferroelectric films*.

[3] http://staff.bath.ac.uk/pyspgc/positron_annihilation_spectrosco.htm

Challenges for Theory

Positron modifies electronic charge density and momentum density.

Annihilation rate of a positron in a free electron gas of number density n:[4]

$$\lambda = nv\sigma_{2\gamma} = \pi n/c^3.$$

Actual annihilation rate is higher, because the positron attracts electrons to it: *contact-density enhancement*.

The positron causes an increase in the momentum density near the Fermi edge: *Kahana enhancement*.[5]

Ultimately, want to calculate annihilation rates and annihilating-pair momentum densities for positrons in real materials. First step: *calculate annihilation rate and momentum density for a positron in a HEG*.

Then use energy data to construct electron–positron correlation functionals, enabling DFT simulations of positrons in real materials.

[4] P. A. M. Dirac, Proc. Cam. Phil. Soc. **26**, 361 (1930).

[5] S. Kahana, Phys. Rev. **129**, 1622 (1963).

Some of the Better Previous Attempts (I)

- **Bethe–Goldstone equation**
  - S. Kahana, Phys. Rev. **129**, 1622 (1963).
- **Tamm–Dancoff approximation**
  - J. Arponen and E. Pajanne, Ann. Phys. **121**, 343 (1979).
- **Fermi hypernetted chain approximation**
  - L. J. Lantto, Phys. Rev. B **36**, 5160 (1987).
  - V. Apaja, S. Denk and E. Krotscheck, Phys. Rev. B **68**, 195118 (2003).
- **Perturbed hypernetted chain approximation**
  - H. Stachowiak, Phys. Rev. B **41**, 12522 (1990).
  - H. Stachowiak and J. Lach, Phys. Rev. B **48**, 9828 (1993).
  - E. Boroński and H. Stachowiak, Phys. Rev. B **57**, 6215 (1998).

Some of the Better Previous Attempts (II)

- **Two-component density functional theory**
  - P. A. Sterne and J. H. Kaiser, Phys. Rev. B **43**, 13892 (1991).

- **Variational quantum Monte Carlo (using plane-wave orbitals)**
  - G. Ortiz, PhD thesis, Swiss Federal Institute of Technology, Lausanne (1992).
  - L. Fraser, PhD thesis, Imperial College, London (1995).

Apologies to all the many other people who have tried their hand at this problem.

Electron–Positron Hamiltonian (I)

Hamiltonian for positron in HEG:

$$\hat{H} = \sum_i \frac{-1}{2}\frac{\partial^2}{\partial \mathbf{r}_i^2} - \frac{1}{2}\frac{\partial^2}{\partial \mathbf{s}^2} - \sum_i \frac{1}{|\mathbf{r}_i - \mathbf{s}|} + \sum_{j>i} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}.$$

Make coordinate transformation suggested by Leung *et al.*[6]

$$\begin{aligned} \mathbf{X} &= \frac{1}{N+1}\left(\mathbf{s} + \sum_{i=1}^{N} \mathbf{r}_i\right) \\ \mathbf{x}_i &= \mathbf{r}_i - \mathbf{s}. \end{aligned}$$

Then Hamiltonian is

$$\hat{H}' = \frac{-1}{2(N+1)}\frac{\partial^2}{\partial \mathbf{X}^2} - \sum_i \left(\frac{\partial^2}{\partial \mathbf{x}_i^2} + \frac{1}{|\mathbf{x}_i|}\right) + \sum_{j>i}\left(-\frac{\partial^2}{\partial \mathbf{x}_i \partial \mathbf{x}_j} + \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|}\right).$$

[6] C. H. Leung, M. J. Stott and C. O. Almbladh, Phys. Lett. **57A**, 26 (1976).

Electron–Positron Hamiltonian (II)

First term on RHS is CoM KE operator. May neglect in ground state.

Left with Hamiltonian for N interacting Fermions of mass $1/2$ a.u. and charge -1 a.u. in the presence of a fixed positive charge of magnitude 1 a.u. at the origin.

There is an extra interaction $\hat{A}$, resembling mass-polarisation.

This term was neglected by Leung *et al.*, who argued that it has only a small effect on the electron–positron correlation energy.

But the term isn't small. For a HEG without a positron, the expectation of the extra interaction is minus half the KE.

Extra Interaction in a One-Electron Theory

Suppose Ψ is a product of determinants of **orthonormal** orbitals $\{\psi_i\}$ for spin-up and spin-down electrons. Then the expectation of the extra interaction is

$$\left\langle \Psi \left| \hat{A} \right| \Psi \right\rangle = -\frac{1}{2} \sum_{i,j} \left[\langle \psi_i | \nabla \psi_i \rangle \cdot \langle \psi_j | \nabla \psi_j \rangle - \delta_{s_i,s_j} \langle \psi_i | \nabla \psi_j \rangle \cdot \langle \psi_j | \nabla \psi_i \rangle \right],$$

where s_i is the spin of particle i.

Direct term vanishes if all orbitals are real or are occupied at both $\mathbf{k}$ and $-\mathbf{k}$. We consider only closed-shell ground states, so the direct term can be neglected.

It is easy to show that the exchange term is only nonzero between bands with the same $\mathbf{k}$ vector. Simpler than exchange term for Coulomb interaction.

Expectation value is much uglier with nonorthogonal orbitals. Avoid ultrasoft pseudopotentials.

Easiest just to use the bare Coulomb potential as we need all-electron orbitals anyway.

Kohn–Sham Equations

Require $\langle\Psi|\hat{T}|\Psi\rangle + \langle\Psi|\hat{A}|\Psi\rangle + E_H[n] + E_{\text{ext}}[n] + E_{\text{xc}}[n]$ to be stationary with respect to variations in ψ_i^*:

$$\begin{aligned}\left[-\nabla^2 + V_H(\mathbf{x}) + V_{\text{ext}}(\mathbf{x}) + V_{\text{xc}}(\mathbf{x})\right]\psi_i(\mathbf{x}) & \\ + \sum_j f_j \delta_{s_i,s_j} \langle\psi_j|\nabla\psi_i\rangle \cdot \nabla\psi_j(\mathbf{x}) &= \mathcal{E}_i\psi_i(\mathbf{x}),\end{aligned}$$

where V_H, V_{ext} and V_{xc} are the Hartree, external (positron) and exchange–correlation potentials, and f_j and $\mathcal{E}_j$ are the occupation number and eigenvalue of state j.

Unlike the Hartree and XC energies, the extra interaction depends directly on the orbital coefficients rather than just the density.

Equations are solved self-consistently by a modified version of the CASTEP[7] plane-wave DFT code: *pCASTEP*.

[7] M. D. Segall, P. J. D. Lindan, M. J. Probert, C. J. Pickard, P. J. Hasnip, S. J. Clark and M. C. Payne, J. Phys. Cond. Matt. **14**, 2717 (2002).

Eigenvalues

Consider a HEG in the transformed coordinate system. Orbitals are $\exp(i\mathbf{G}\cdot\mathbf{x})/\sqrt{V}$. Eigenvalue of one-electron extra interaction operator:

$$\begin{aligned}\exp(-i\mathbf{G}\cdot\mathbf{x})\hat{a}_1\exp(i\mathbf{G}\cdot\mathbf{x}) &= \sum_{\mathbf{G}'}\frac{f_{\mathbf{G}'}}{V}\int\exp[i(\mathbf{G}-\mathbf{G}')\cdot(\mathbf{x}'-\mathbf{x})]i\mathbf{G}\,d\mathbf{x}'\cdot i\mathbf{G}' \\ &= -G^2 f_{\mathbf{G}}.\end{aligned}$$

So the Kohn–Sham eigenvalues are

$$\varepsilon_{\mathbf{G}} = G^2(1-f_{\mathbf{G}}).$$

Eigenvalues are zero for occupied states and G^2 for unoccupied states. In the infinite-system limit there is a discontinuity of magnitude k_F^2 in the energy band at k_F.

Adding the positron does not remove the gap.

System is a metal with a huge band gap!

Getting pCASTEP to Converge

Large gap quickly forces occupancies to be zero or one. There is a huge energy cost to fractional occupancy. Must ensure electron number is a magic number for system with unfolded $\mathbf{k}$ points.

Calculations with multiple-$\mathbf{k}$ points often get stuck in excited states because the initial (random) number of occupied states at each $\mathbf{k}$ gets frozen in.

Solution: just work at Γ. (Shell-filling effects mostly cancel out of energy differences and don't affect pair correlation functions very much anyway.)

Default density mixing scheme in CASTEP (Broyden) is poor. Other mixing schemes (e.g., Pulay) work better.

Successful strategies: (A) iterate orbital coefficients to self-consistency every time the density is updated; (B) converge the orbitals in the absence of the extra interaction, then switch on extra interaction and re-converge.

Relaxation Energy

If there is no electron–positron correlation then the positron occupies its zero-momentum ground state. *In this case, the energy of the HEG+positron is the same as energy of the HEG without the positron.*

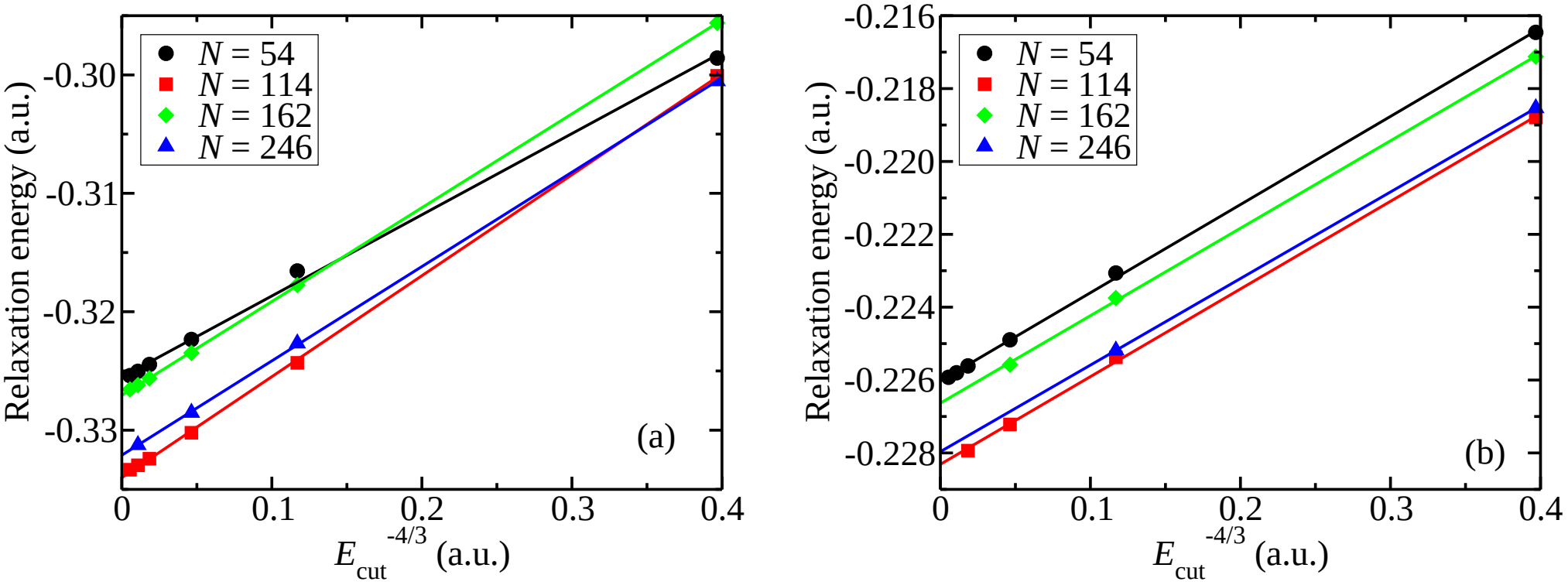
So the electron–positron correlation energy is the difference of the energy of the N-electron HEG+positron and the N-electron HEG.

Electron–positron correlation energy is called the *relaxation energy*.

Calculations should be performed in a cell of volume $(4/3)\pi r_s^3(N-1)$, so the electron density of the HEG+positron at the edge of the cell is the same as that of a HEG of density parameter r_s. Reduces finite-size errors.

Having calculated the relaxation energy, we can fit a function to our data and hence parametrise an electron–positron correlation functional for use in DFT studies of positrons in real materials.

Finite-Basis Error in the Relaxation Energy

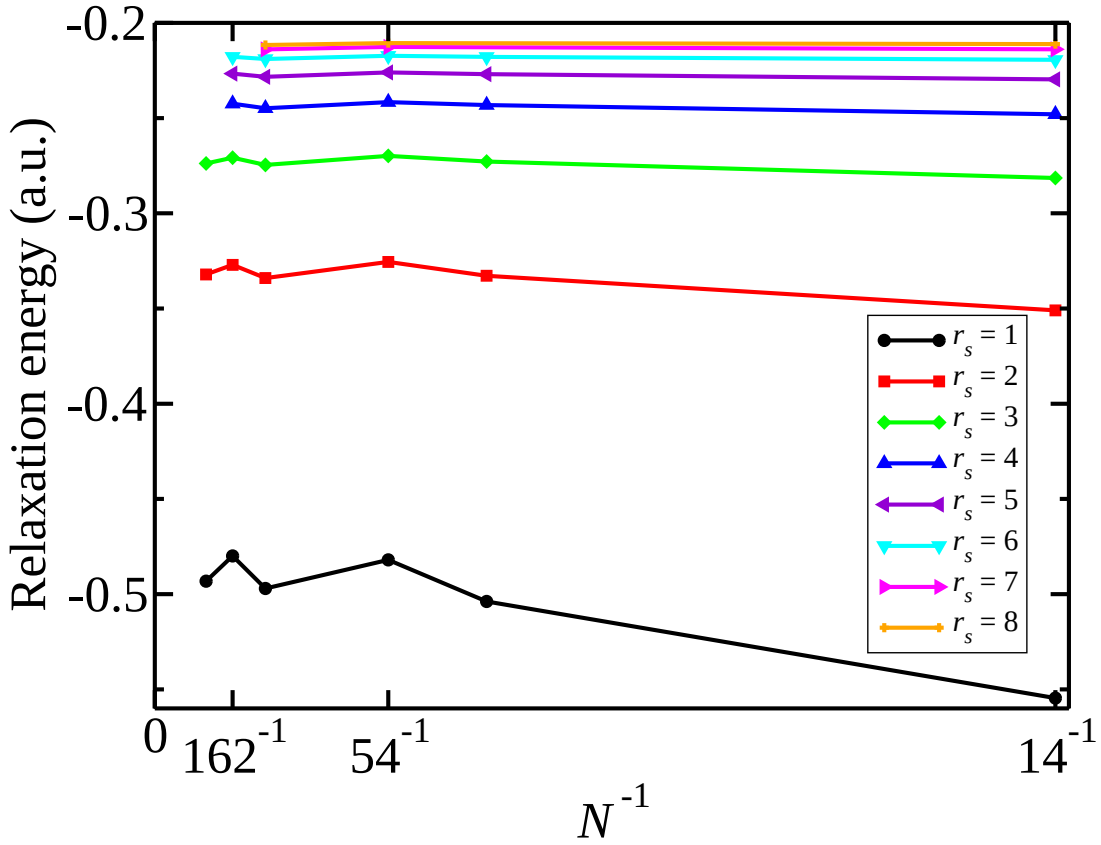


Relaxation energy against plane-wave cutoff energy $E_{\rm cut}$ at $r_s = 2$ and 5.

Extrapolate to basis-set completeness by assuming error goes as $E_{\rm cut}^{-4/3}$.

Still need to deal with finite-size errors.

Finite-Size Error in the Relaxation Energy



Relaxation energy (extrap. to basis-set completeness) against number of electrons N.

For small N, systematic errors due to the interaction of images of the positron are visible, especially at high density.

Above this, only oscillatory shell-filling effects are visible. Average over relaxation energies at highest three N available at each density.

Annihilating-Pair Momentum Density (I)

CoM and difference coordinates: $\bar{\mathbf{r}}_i \equiv (\mathbf{r}_i + \mathbf{s})/2$ and $\delta\mathbf{r}_i \equiv \mathbf{r}_i - \mathbf{s}$.

Electron–positron centre-of-mass momentum wave function:

$$\tilde{\Psi}(\bar{\mathbf{p}}_1, \delta\mathbf{r}_1; \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{V} \int \exp(-i\bar{\mathbf{p}}_1 \cdot \bar{\mathbf{r}}_1) \Psi(\bar{\mathbf{r}}_1, \delta\mathbf{r}_1; \mathbf{r}_2, \ldots, \mathbf{r}_N)\, d\bar{\mathbf{r}}_1,$$

Assumption: *distribution of annihilating-pair momenta same as distribution of CoM momenta when positron coincides with an electron of opposite spin*.

Unnormalised distribution of CoM momentum for positron annihilating with electron 1:

$$\int \cdots \int |\tilde{\Psi}(\bar{\mathbf{p}}_1, \mathbf{0}; \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2\, d\mathbf{r}_2 \ldots d\mathbf{r}_N.$$

Annihilating-Pair Momentum Density (II)

Normalise and use antisymmetry of wave function to get momentum density:

$$\begin{aligned}\rho_\uparrow(\bar{\mathbf{p}}) &= \frac{\int\cdots\int|\tilde{\Psi}(\bar{\mathbf{p}},\mathbf{0};\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2\,d\mathbf{r}_2\ldots d\mathbf{r}_N}{\sum_{\bar{\mathbf{p}}}\int\cdots\int|\tilde{\Psi}(\bar{\mathbf{p}},\mathbf{0};\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2\,d\mathbf{r}_2\ldots d\mathbf{r}_N} \\ &= \frac{\int\cdots\int\left|\int\exp(-i\bar{\mathbf{p}}\cdot\mathbf{r}_1)\Psi(\mathbf{r}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\,d\mathbf{r}_1\right|^2 d\mathbf{r}_2\ldots d\mathbf{r}_N}{V\int\cdots\int|\Psi(\mathbf{r}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)|^2\,d\mathbf{r}_1\ldots d\mathbf{r}_N}.\end{aligned}$$

Now suppose

$$\begin{aligned}\Psi(\mathbf{s};\mathbf{r}_1,\ldots,\mathbf{r}_N) = \frac{1}{\sqrt{N_\uparrow!N_\downarrow!}}&\begin{vmatrix}\phi_1^\uparrow(\mathbf{r}_1-\mathbf{s}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_1-\mathbf{s})\\ \vdots & & \vdots\\ \phi_1^\uparrow(\mathbf{r}_{N_\uparrow}-\mathbf{s}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_{N_\uparrow}-\mathbf{s})\end{vmatrix}\\ \times&\begin{vmatrix}\phi_1^\downarrow(\mathbf{r}_{N_\uparrow+1}-\mathbf{s}) & \cdots & \phi_{N_\downarrow}^\downarrow(\mathbf{r}_{N_\uparrow+1}-\mathbf{s})\\ \vdots & & \vdots\\ \phi_1^\downarrow(\mathbf{r}_N-\mathbf{s}) & \cdots & \phi_{N_\downarrow}^\downarrow(\mathbf{r}_N-\mathbf{s})\end{vmatrix}.\end{aligned}$$

Annihilating-Pair Momentum Density (III)

The numerator of the momentum density may be shown to be

$$\rho_{\uparrow u}(\bar{\mathbf{p}}) = \int e^{-i\bar{\mathbf{p}}\cdot\mathbf{R}} \int \cdots \int \sum_{i=1}^{N_\uparrow}\sum_{j=1}^{N_\uparrow} (-1)^{i+j} \phi_i^{\uparrow *}(\mathbf{0})\phi_j^{\uparrow}(\mathbf{0}) M_{1i}N_{1j}\, d\mathbf{r}_2 \ldots d\mathbf{r}_{N_\uparrow}$$
$$\times \frac{V}{N_\uparrow!} \begin{vmatrix} \int \phi_1^{\downarrow *}(\mathbf{r})\phi_1^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} & \cdots & \int \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r})\phi_1^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} \\ \vdots & & \vdots \\ \int \phi_1^{\downarrow *}(\mathbf{r})\phi_{N_\downarrow}^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} & \cdots & \int \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r})\phi_{N_\downarrow}^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} \end{vmatrix} d\mathbf{R},$$

where M_{ij} and N_{ij} are the (i,j)th minors of

$$\begin{vmatrix} \phi_1^{\uparrow *}(\mathbf{0}) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{0}) \\ \phi_1^{\uparrow *}(\mathbf{r_2}) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{r}_2) \\ \vdots & & \vdots \\ \phi_1^{\uparrow *}(\mathbf{r}_{N_\uparrow}) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{r}_{N_\uparrow}) \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} \phi_1^{\uparrow}(\mathbf{0}) & \cdots & \phi_{N_\uparrow}^{\uparrow}(\mathbf{0}) \\ \phi_1^{\uparrow}(\mathbf{r_2}-\mathbf{R}) & \cdots & \phi_{N_\uparrow}^{\uparrow}(\mathbf{r}_2-\mathbf{R}) \\ \vdots & & \vdots \\ \phi_1^{\uparrow}(\mathbf{r}_{N_\uparrow}-\mathbf{R}) & \cdots & \phi_{N_\uparrow}^{\uparrow}(\mathbf{r}_{N_\uparrow}-\mathbf{R}) \end{vmatrix}.$$

Annihilating-Pair Momentum Density (IV)

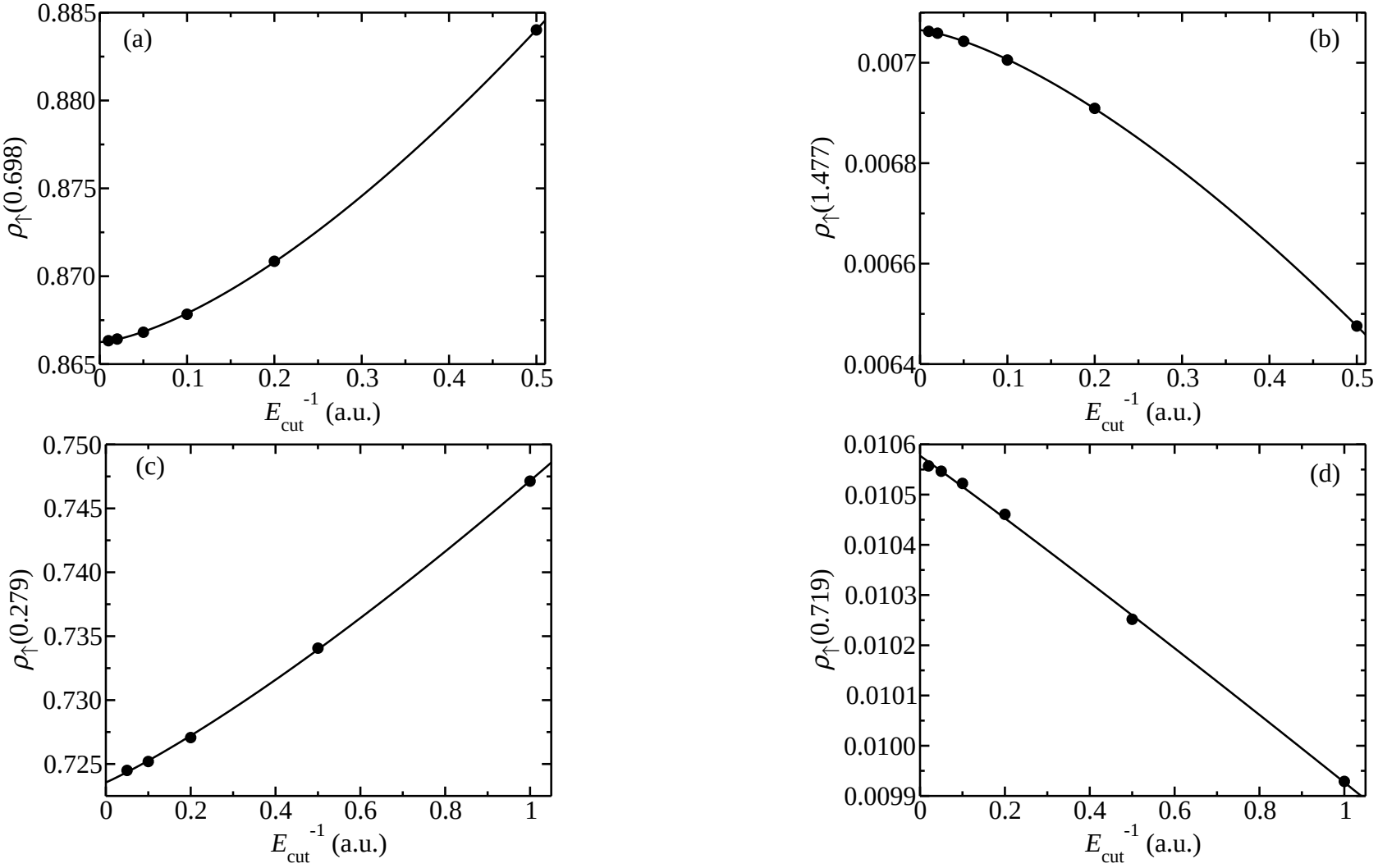
For each $i, j \in \{1, \ldots, N_\uparrow\}$, we can use the overlap integral theorem to determine a $(N_\uparrow - 1) \times (N_\uparrow - 1)$ matrix $B^{\mathbf{R}}(i,j)$ such that

$$\det\left(B^{\mathbf{R}}(i,j)\right) = \frac{1}{(N_\uparrow - 1)!} \int \cdots \int M_{1i} N_{1j}\, d\mathbf{r}_2 \ldots d\mathbf{r}_{N_\uparrow}.$$

So unnormalised annihilating-pair momentum density is

$$\begin{aligned}
\rho_{\uparrow u}(\bar{\mathbf{p}}) \quad = \quad & \int \exp(-i\bar{\mathbf{p}} \cdot \mathbf{R}) \sum_{i=1}^{N_\uparrow} \sum_{j=1}^{N_\uparrow} (-1)^{i+j} \phi_i^{\uparrow *}(\mathbf{0}) \phi_j^{\uparrow}(\mathbf{0}) \det\left(B^{\mathbf{R}}(i,j)\right) \\
& \times \begin{vmatrix} \int \phi_1^{\downarrow *}(\mathbf{r}) \phi_1^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} & \cdots & \int \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r}) \phi_1^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} \\ \vdots & & \vdots \\ \int \phi_1^{\downarrow *}(\mathbf{r}) \phi_{N_\downarrow}^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} & \cdots & \int \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r}) \phi_{N_\downarrow}^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} \end{vmatrix} d\mathbf{R}.
\end{aligned}$$

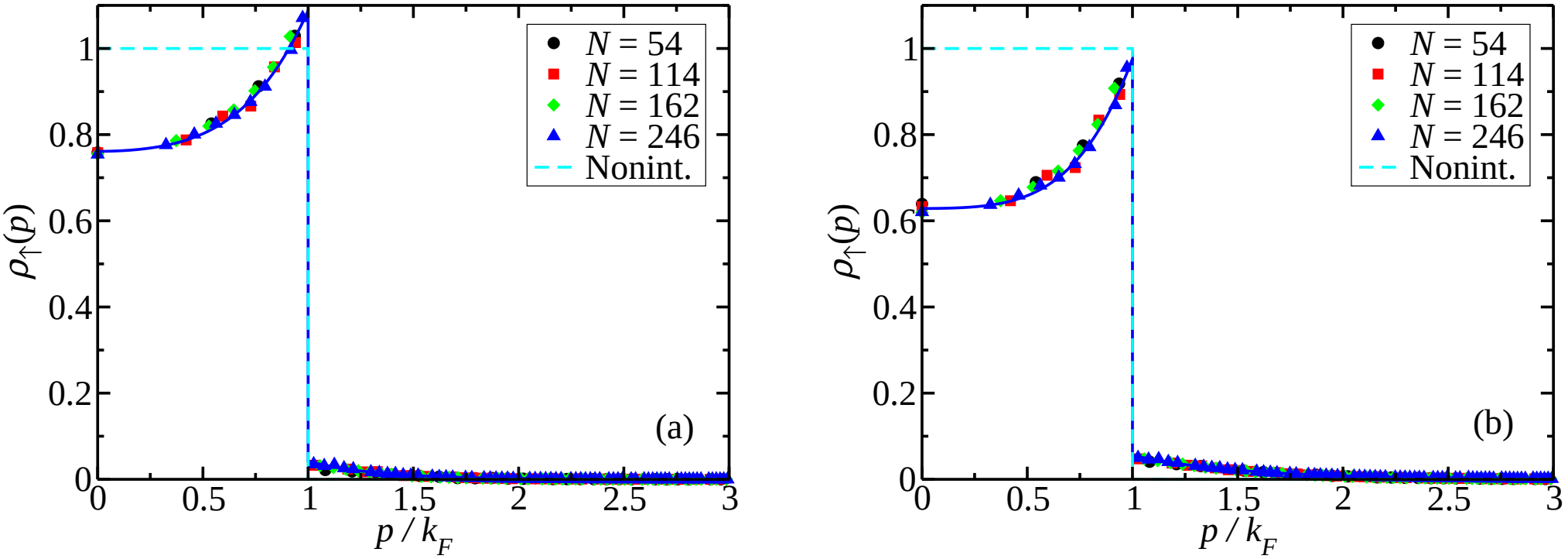
Finite-Basis Error in the Momentum Density



MDs above and below the Fermi edge at different system sizes and at $r_s = 2$ and 5.

Extrapolate to basis-set completeness by assuming error goes as $aE_{\rm cut}^{-1} + bE_{\rm cut}^{-3/2}$.

Finite-Size Error in the Momentum Density



MDs extrapolated to basis-set completeness at $r_s = 2$ and 5.

MDs reasonably well converged with respect to N.

Fit model MD to data at largest system size available at each density.

Tail of MD falls off exponentially.

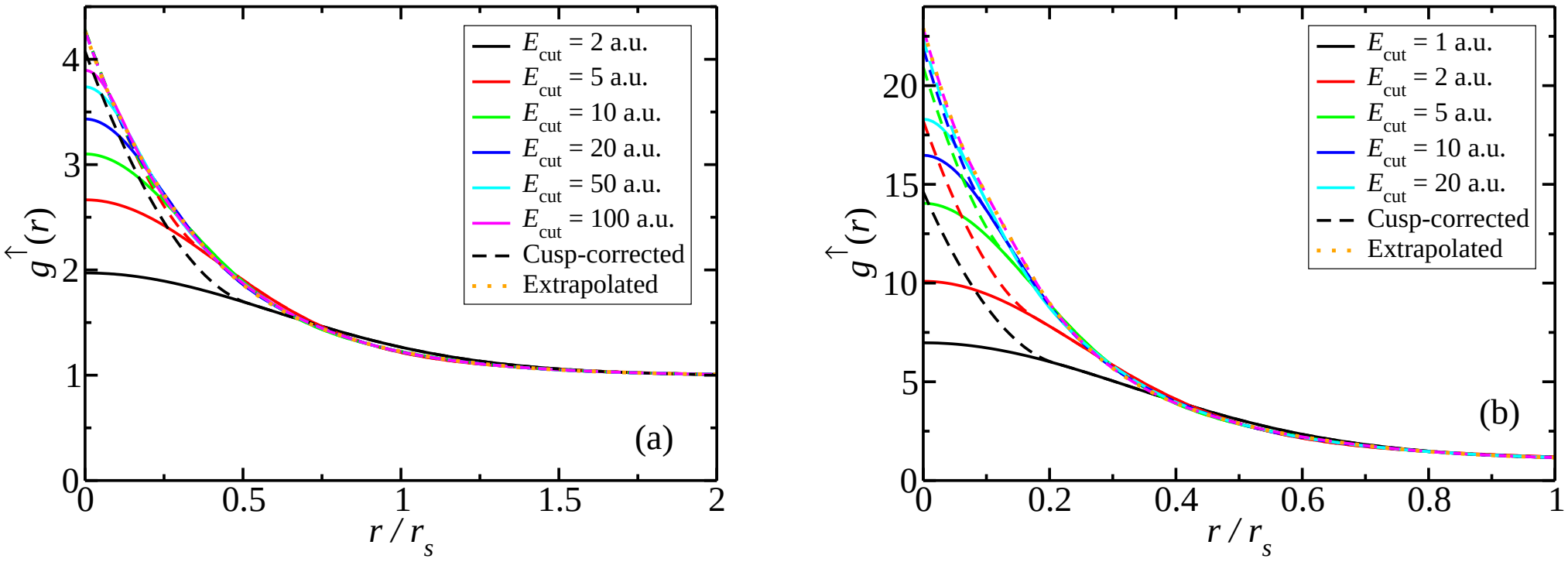
Electron–Positron Pair-Correlation Function

Spin-down positron–spin-up electron pair-correlation function:

$$
\begin{aligned}
g^{\uparrow}(\mathbf{r},\mathbf{s}) &= \frac{\rho_{1p}^{\uparrow}(\mathbf{r},\mathbf{s})}{\rho_{1}^{\uparrow}(\mathbf{r})\rho_{p}(\mathbf{s})} \\
&= V^2 \frac{\int\cdots\int |\Psi(\mathbf{s};\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2\, d\mathbf{r}_2\ldots d\mathbf{r}_N}{\int\cdots\int\int |\Psi(\mathbf{s};\mathbf{r}_1,\ldots,\mathbf{r}_N)|^2\, d\mathbf{r}_1\ldots d\mathbf{r}_N\, d\mathbf{s}} \\
&= \frac{V^2}{N_{\uparrow}} \sum_i \frac{|\phi_i^{\uparrow}(\mathbf{r}-\mathbf{s})|^2}{\langle \phi_i^{\uparrow}|\phi_i^{\uparrow}\rangle}.
\end{aligned}
$$

The electron–positron PCF is proportional to the electronic charge density in the transformed system.

Finite-Basis Errors in the PCF



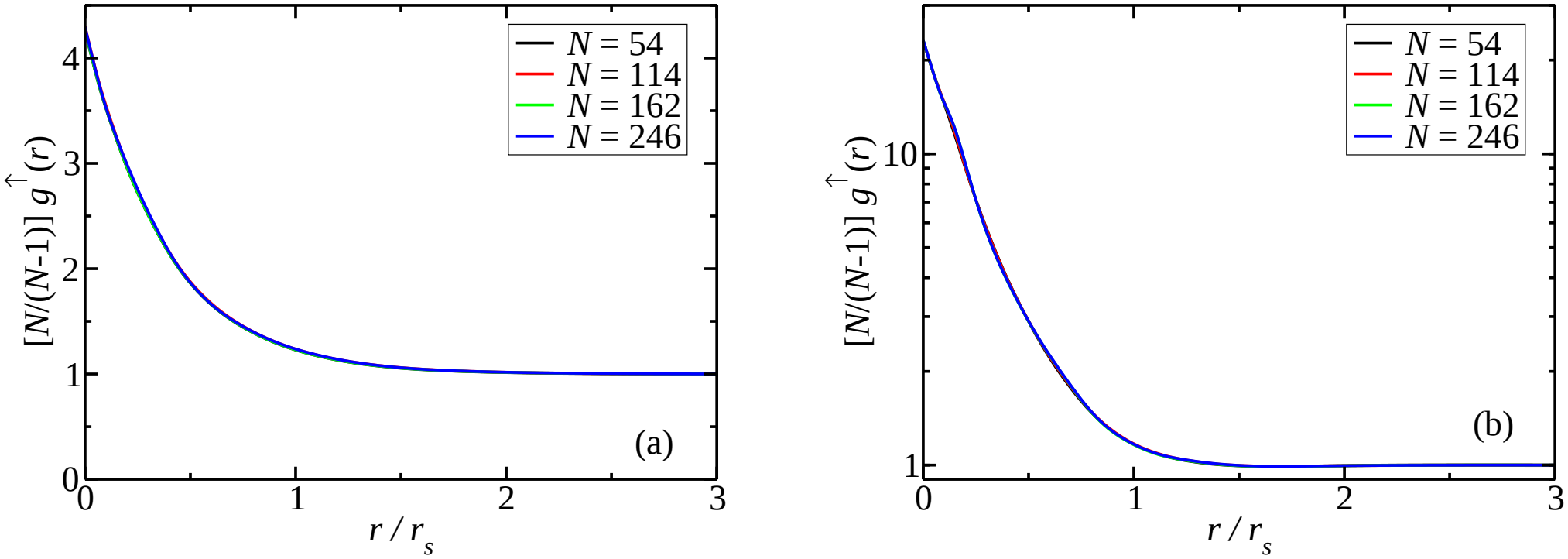
PCFs for $N = 114$ electrons at $r_s = 2$ and 5.

Large finite-basis errors, because Kimball cusp condition $(\partial \bar{g}^{\uparrow}/\partial r)_0 = -g^{\uparrow}(0)$ is violated.

Improve convergence by adding a cusp-correction function $h(r) = a(r - r_{\rm cut})^2$, where a is determined by the Kimball cusp condition and $r_{\rm cut}$ is chosen to mimimise the maximum of $(\bar{g}^{\uparrow} + \partial \bar{g}^{\uparrow}/\partial r)^2$ in $0 \le r \le r_{\rm cut}$.

Extrapolate to basis-set completeness assuming error goes as $aE_{\rm cut}^{-1} + bE_{\rm cut}^{-2}$.

Finite-Size Errors in the PCF



PCFs extrapolated to basis-set completeness at $r_s = 2$ and 5.

Multiply by $N/(N-1)$ to get PCF to go to 1 at edge of finite cell.

Converged with respect to system size. Use results with $N = 162$ electrons.

Contact-Density Enhancement and Annihilation Rate

Effective density of spin-up electrons at the positron:

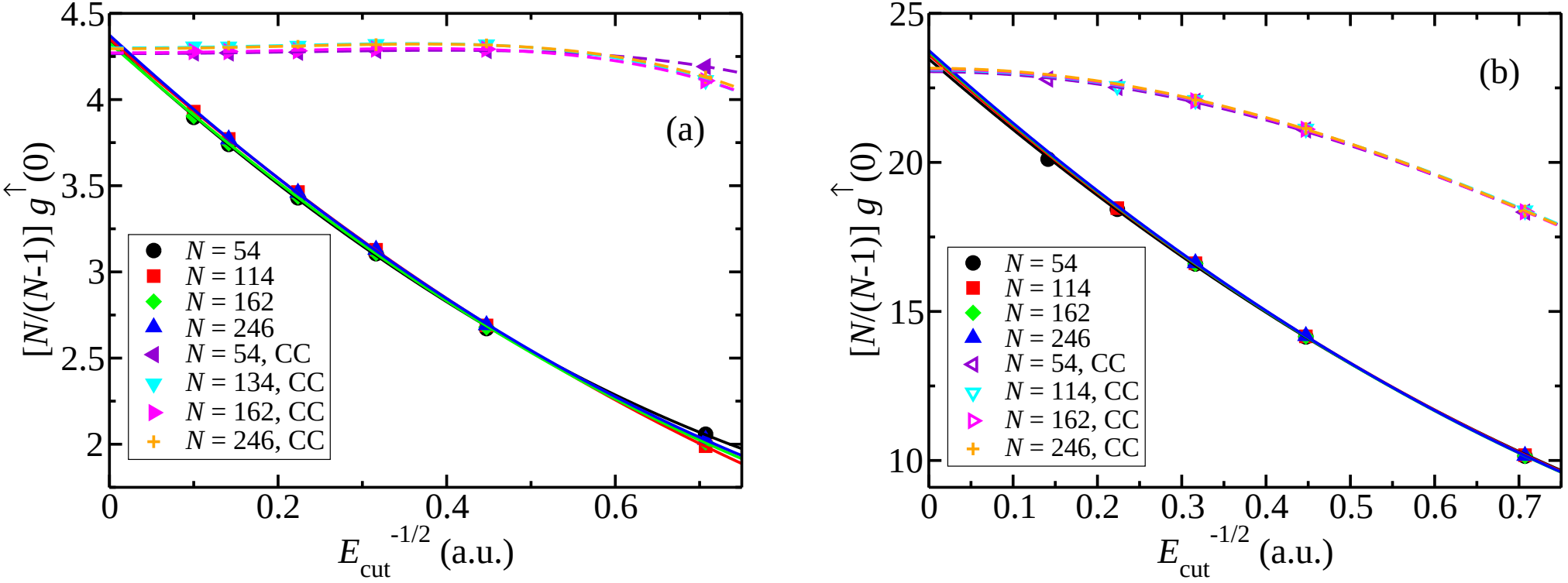
$$n_{\text{eff}}^{\uparrow} = \frac{N_{\uparrow}}{V} g^{\uparrow}(\mathbf{0}).$$

This *contact density* should be used to calculate annihilation rate using the 2-photon annihilation cross-section.

Annihilation rate for spin-up electrons with a spin-down positron:

$$\lambda = \frac{3g(\mathbf{0})}{4c^3 r_s^3}.$$

Finite-Basis and Finite-Size Errors in the Contact PCF

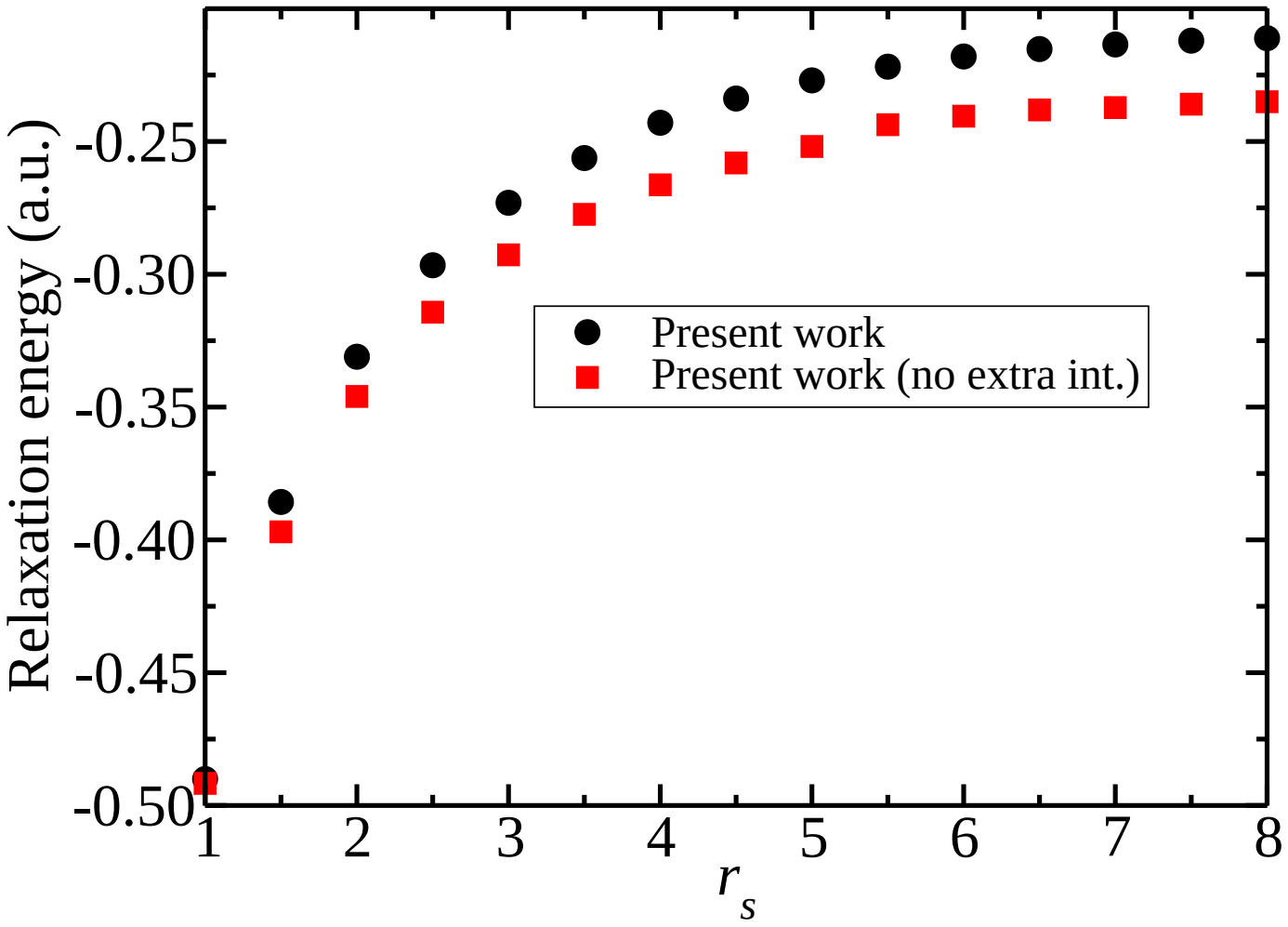


Contact PCFs at $r_s = 2$ and 5.

Extrapolate non-cusp-corrected $g(0)$ to basis-set completeness assuming error goes as $aE_{\mathrm{cut}}^{-1/2} + bE_{\mathrm{cut}}^{-1}$.

Multiply by $N/(N-1)$ and average data with $N > 100$.

Results (I): Relaxation Energy



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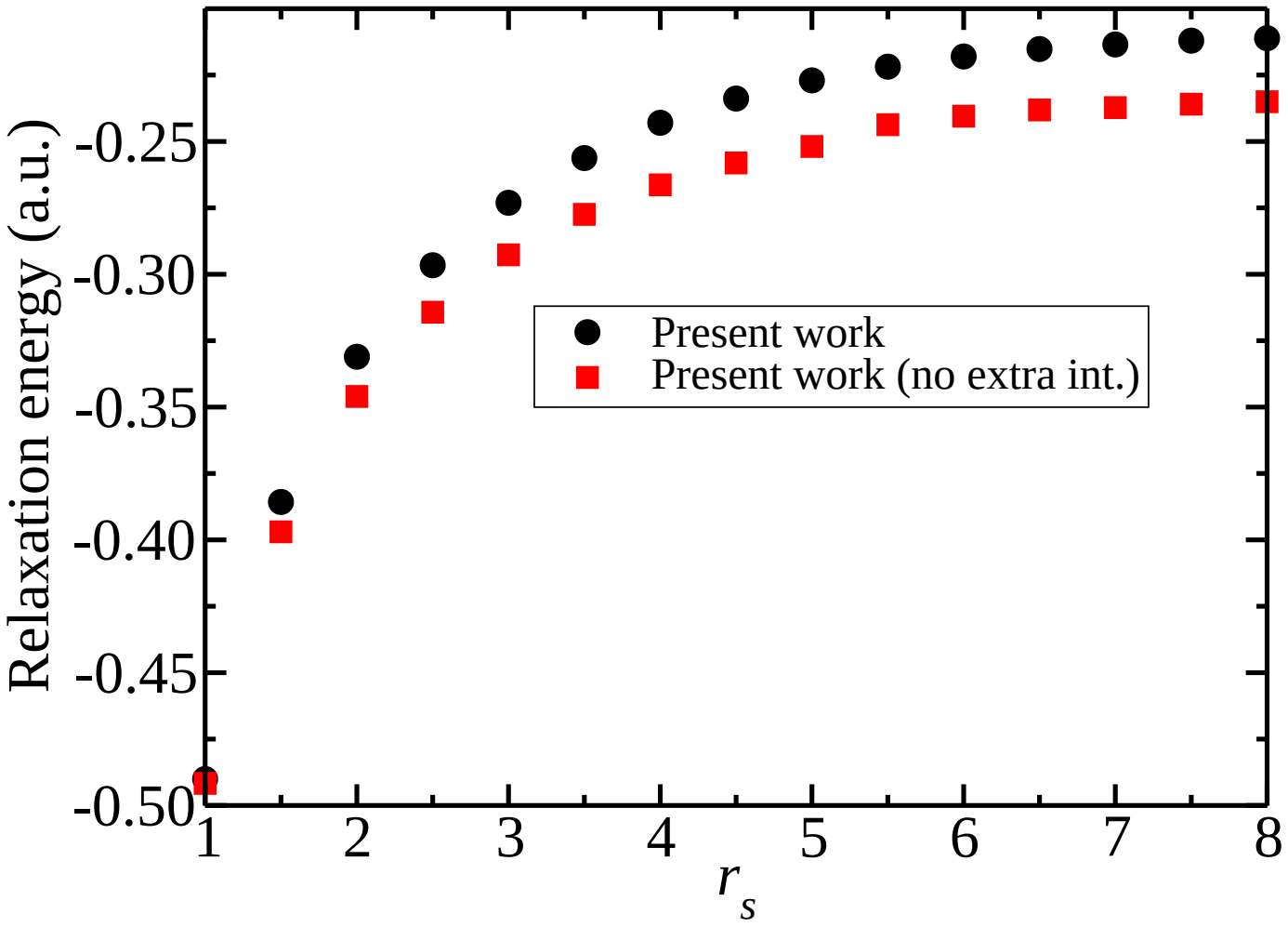

- *Extra interaction makes a small but significant difference to the relaxation energy.*

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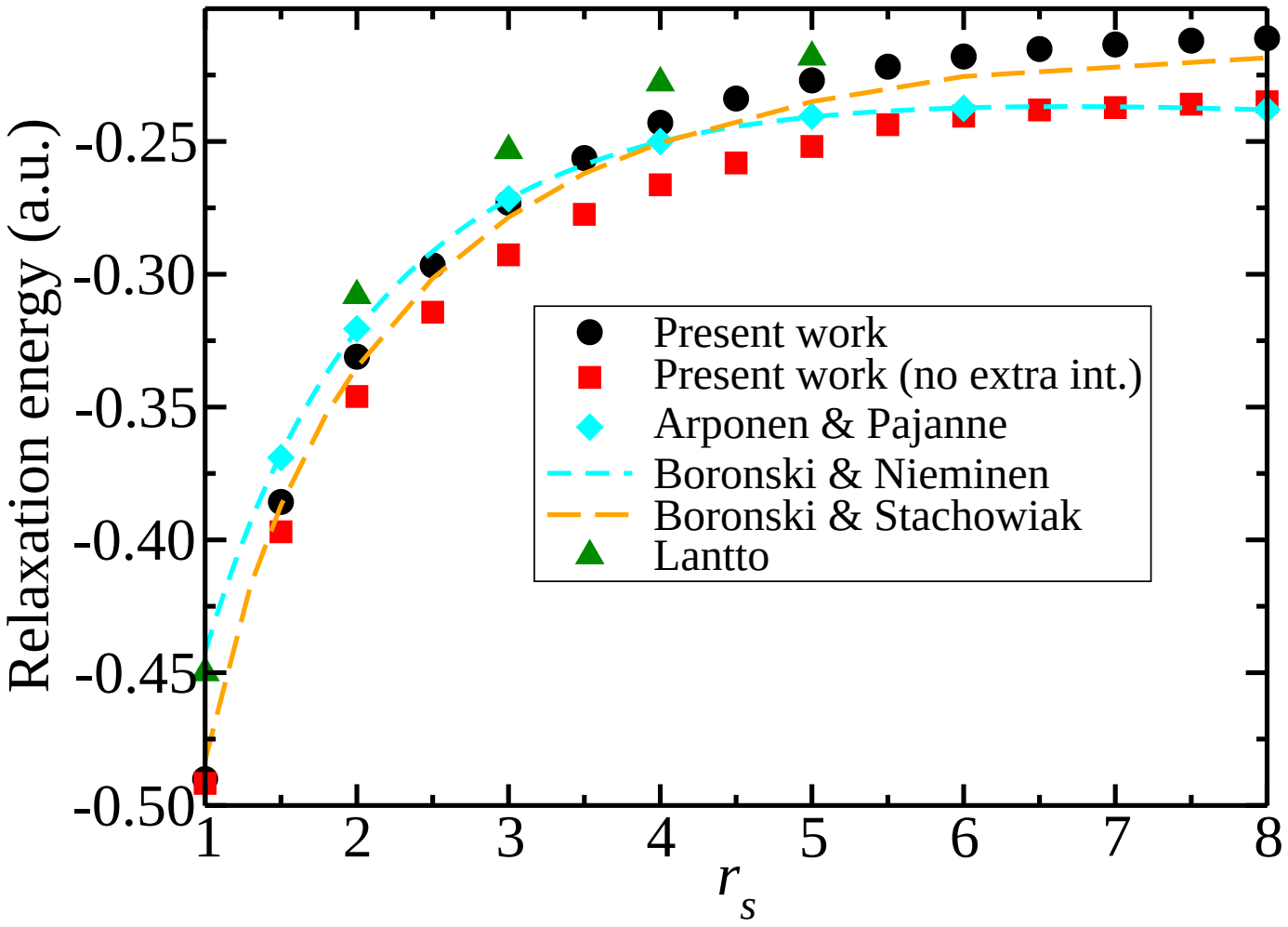

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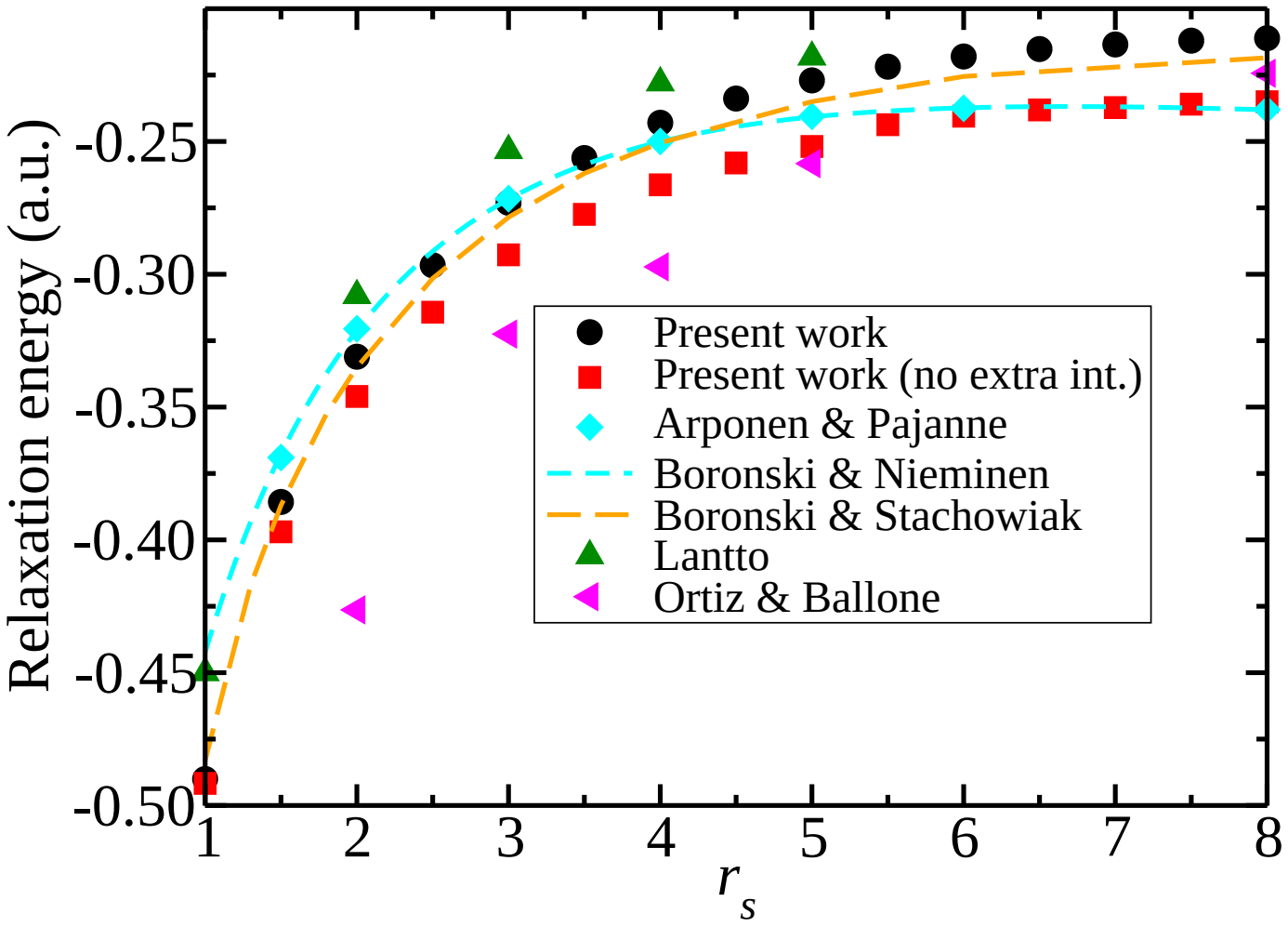

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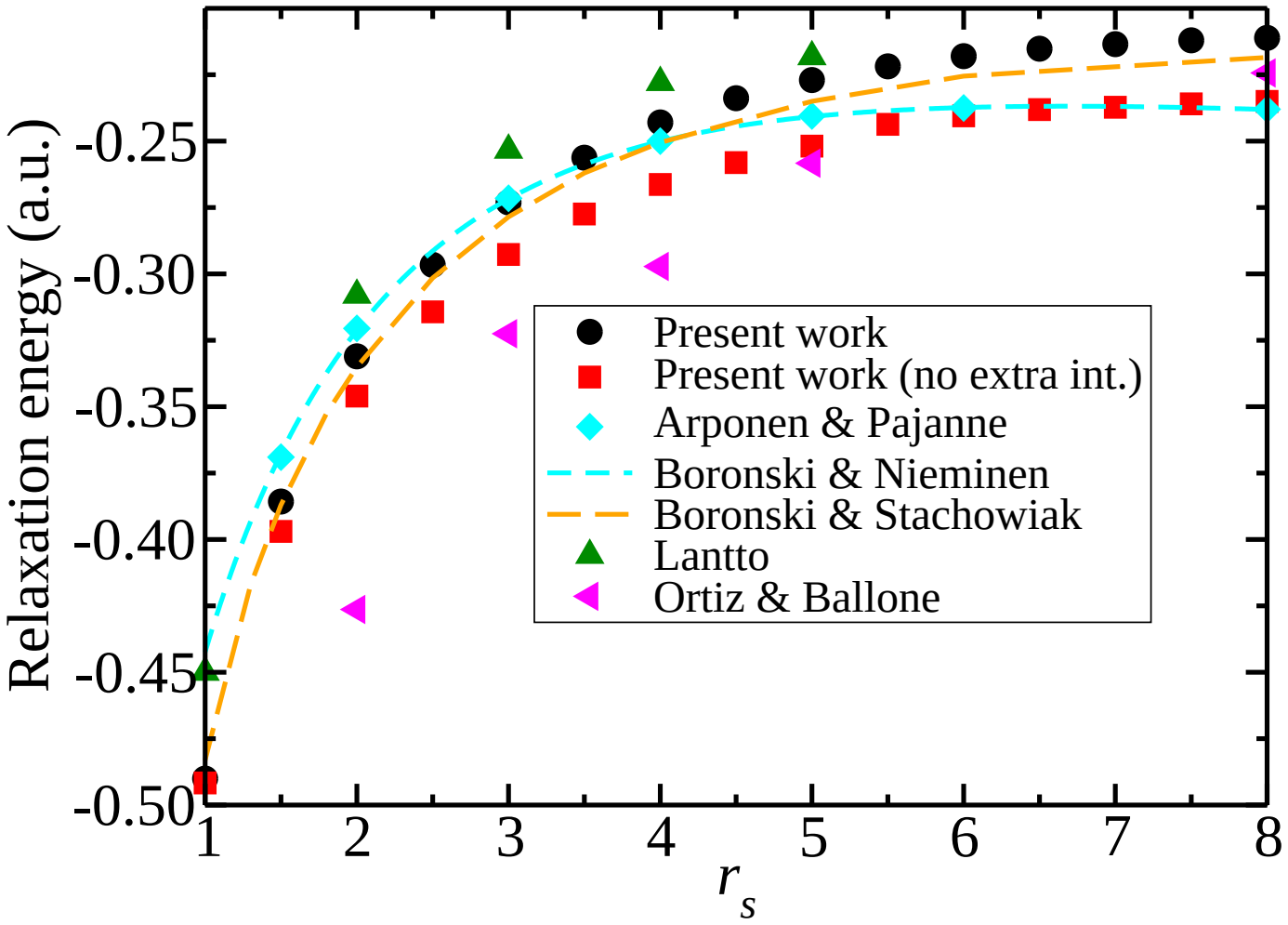

- *Extra interaction makes a small but significant difference to the relaxation energy.*
- *Our results are in reasonable agreement with Boroński and Stachowiak.*

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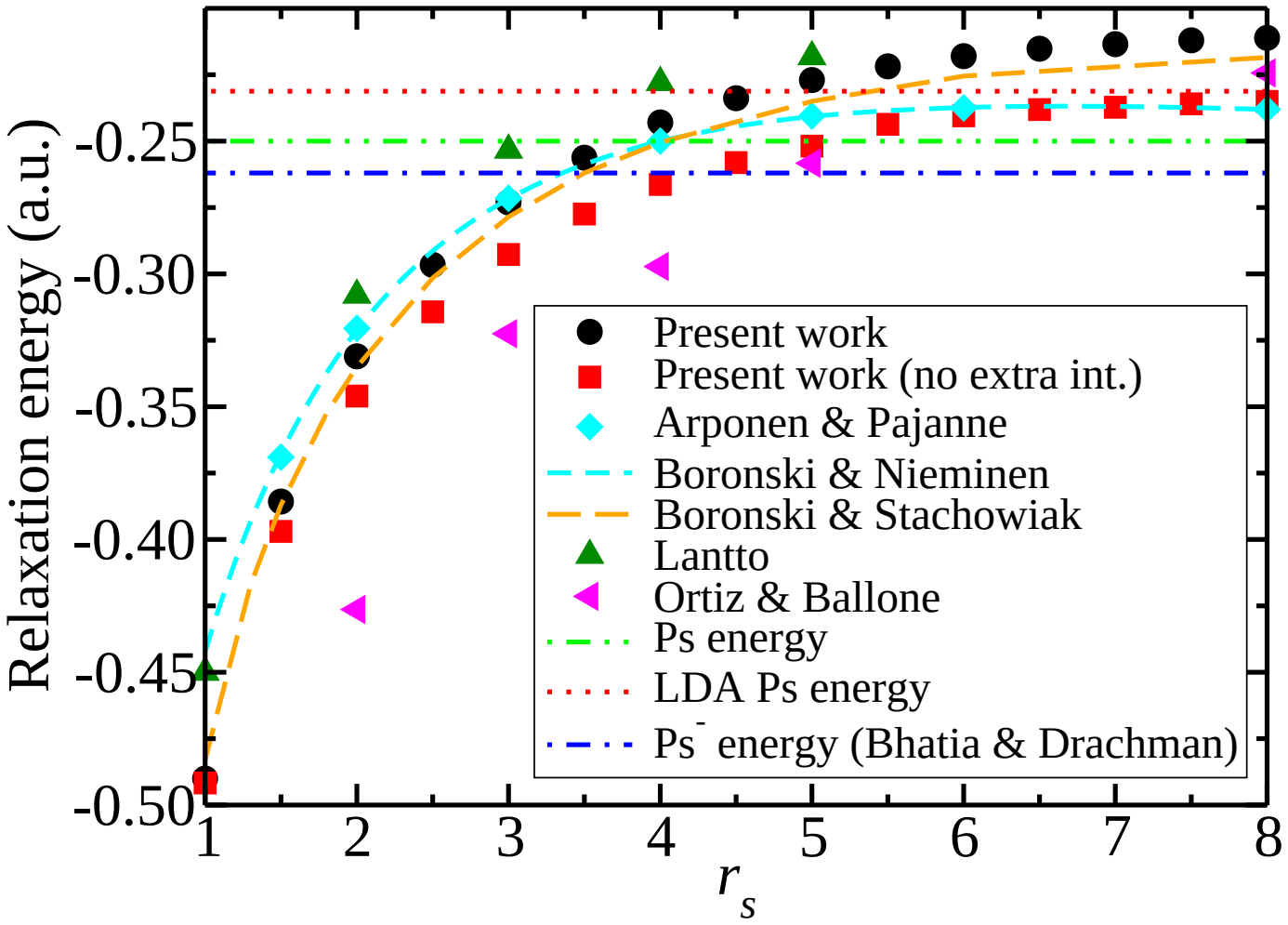

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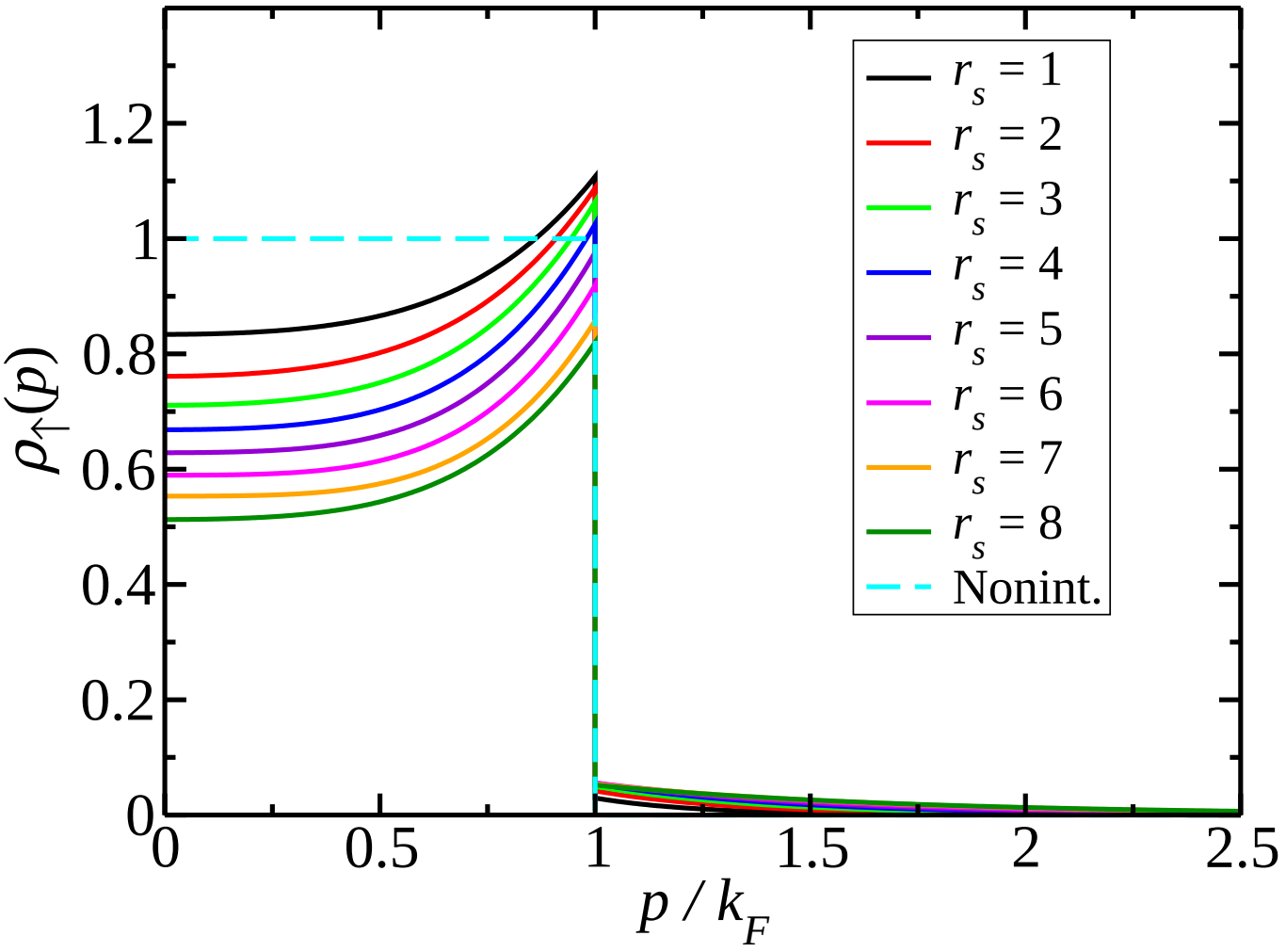
Results (II): Annihilating-Pair Momentum Density



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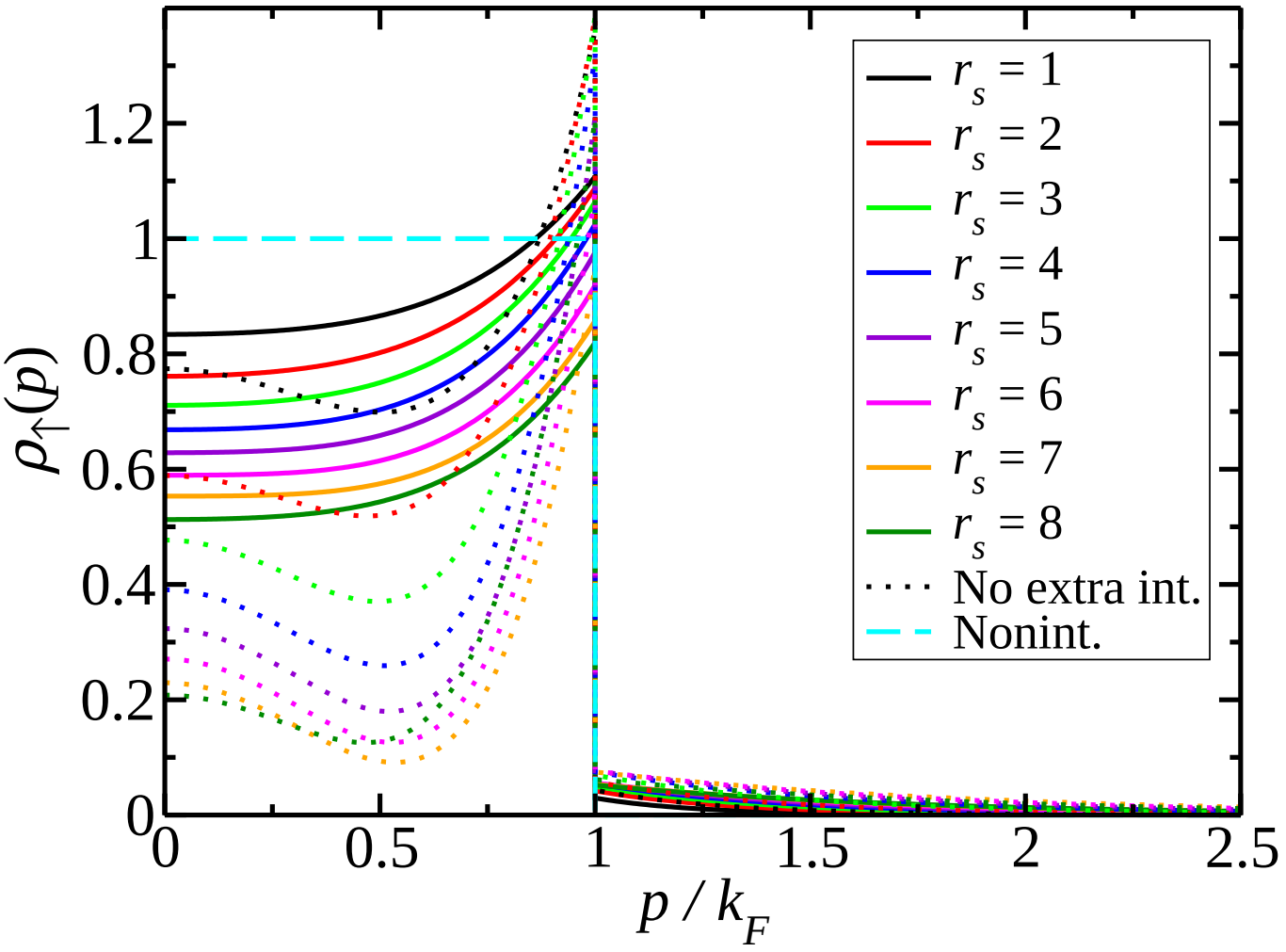

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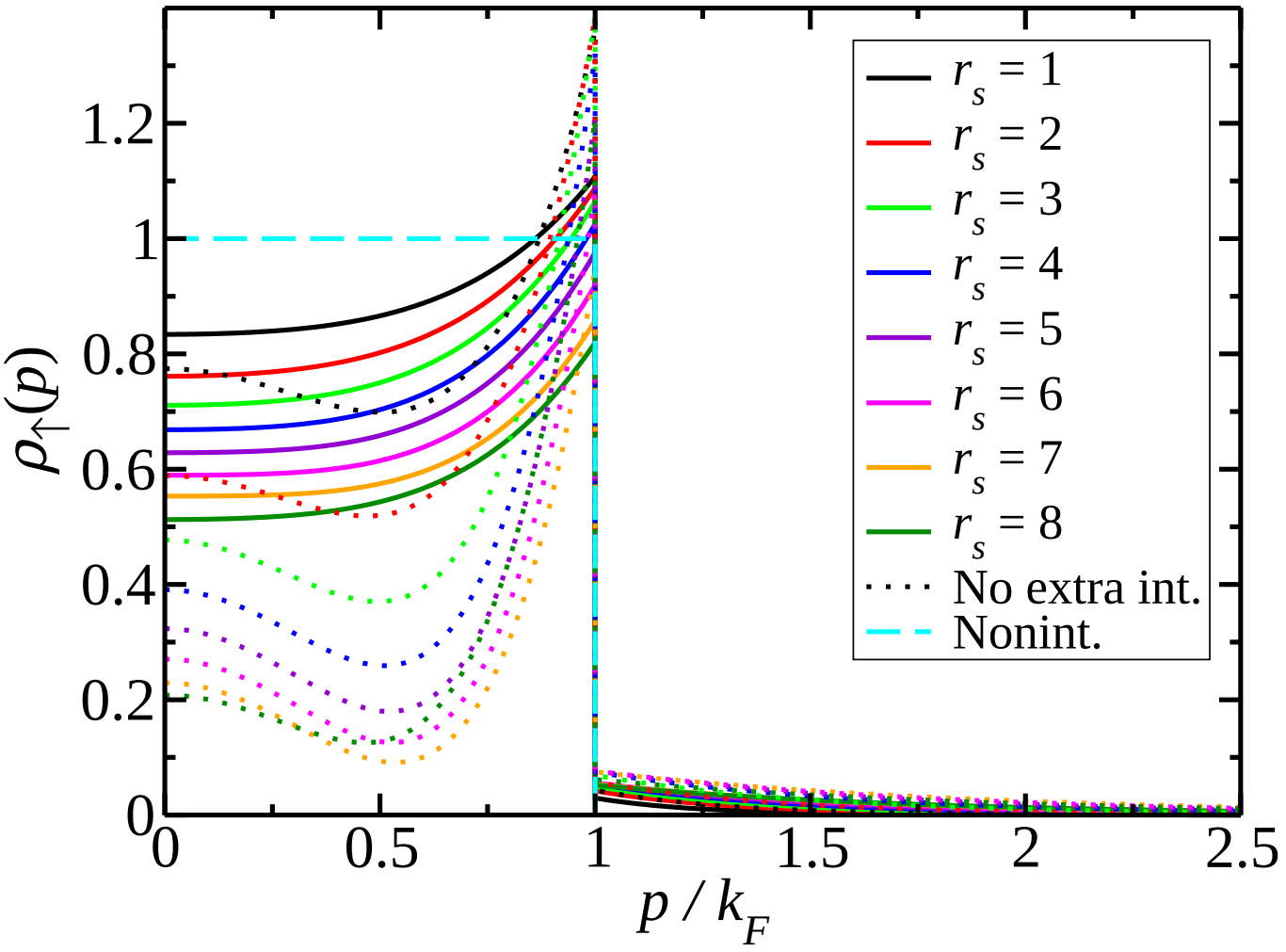

- *The extra interaction is clearly needed when calculating the MD.*

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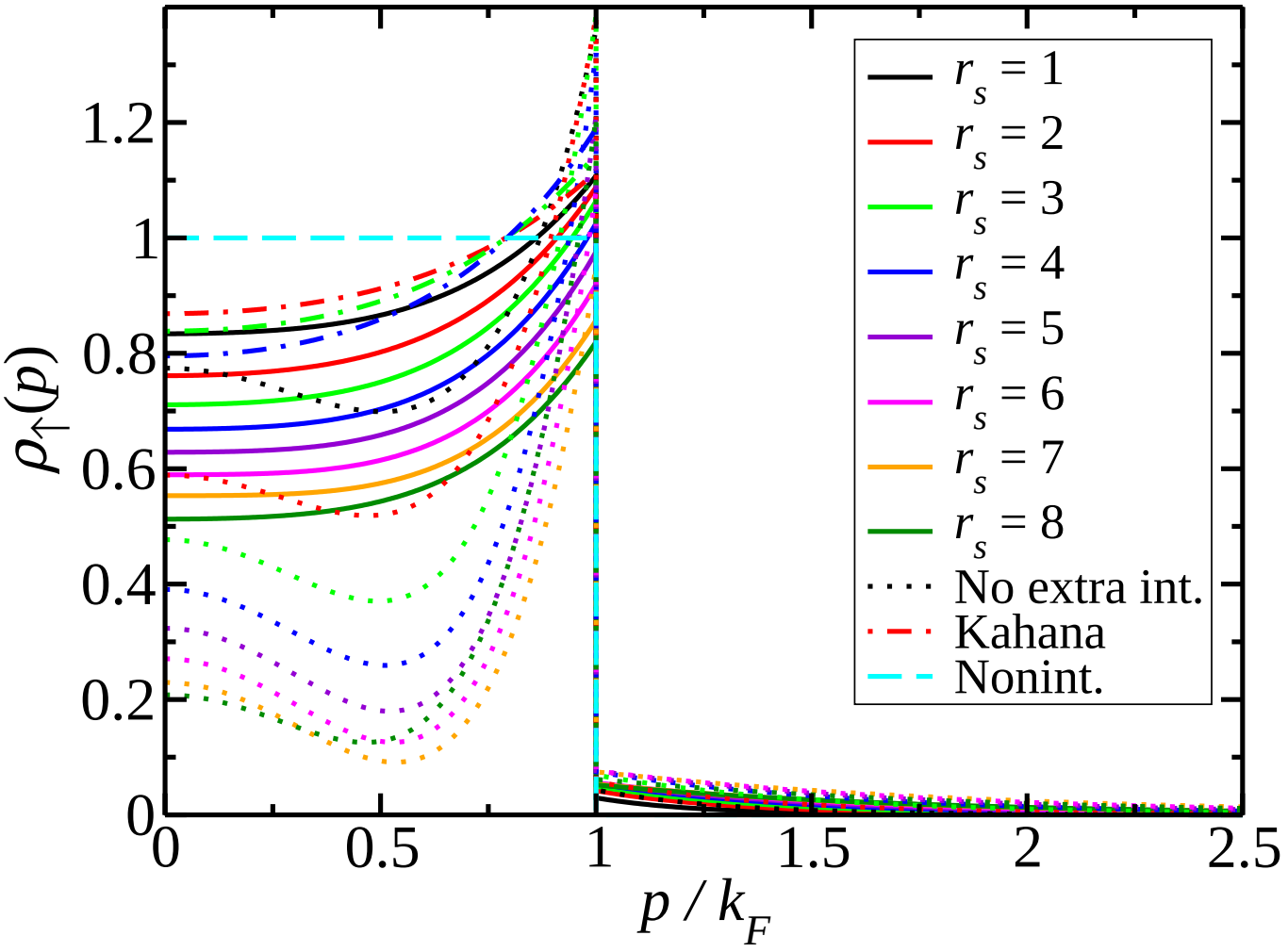

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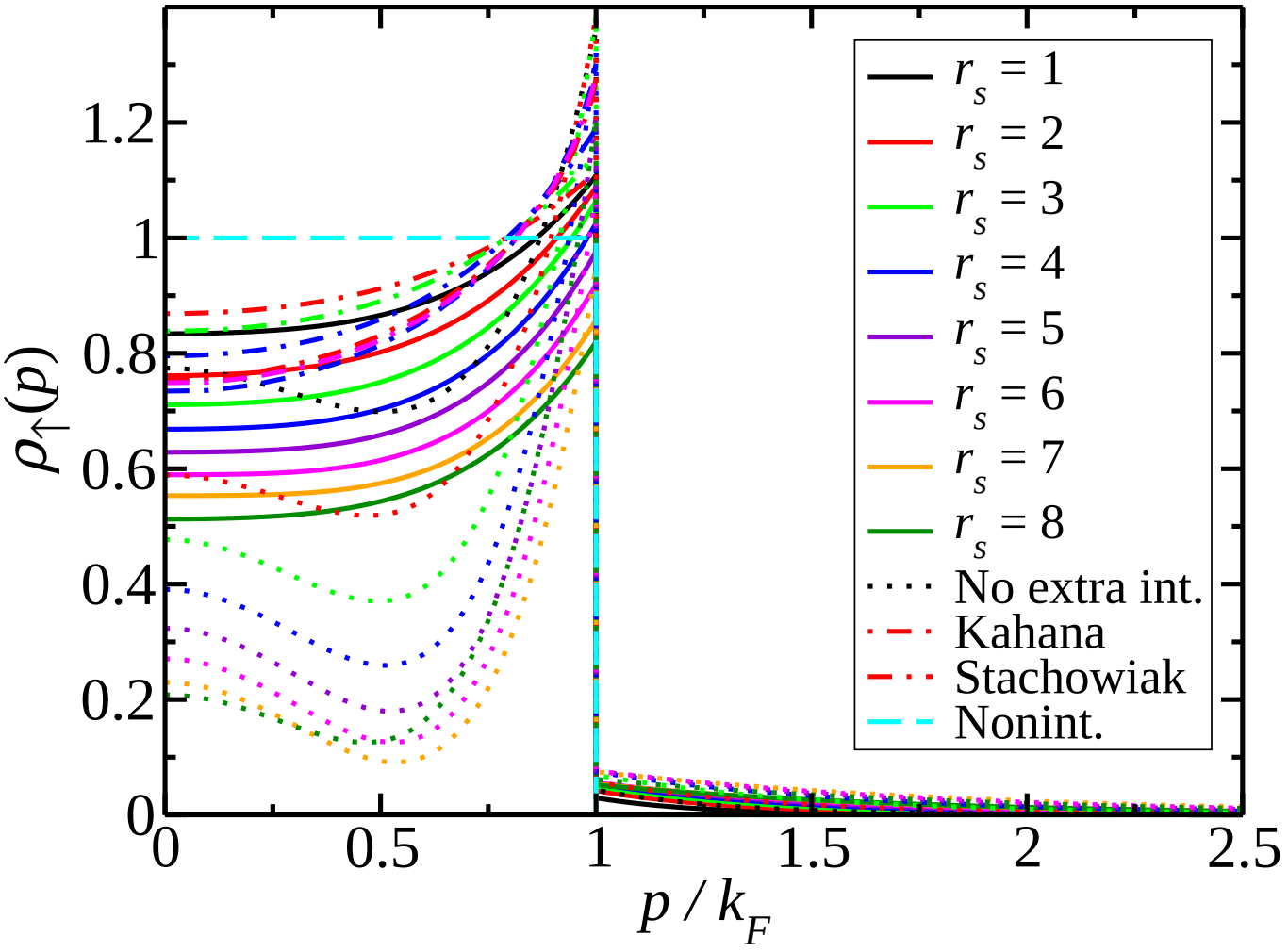

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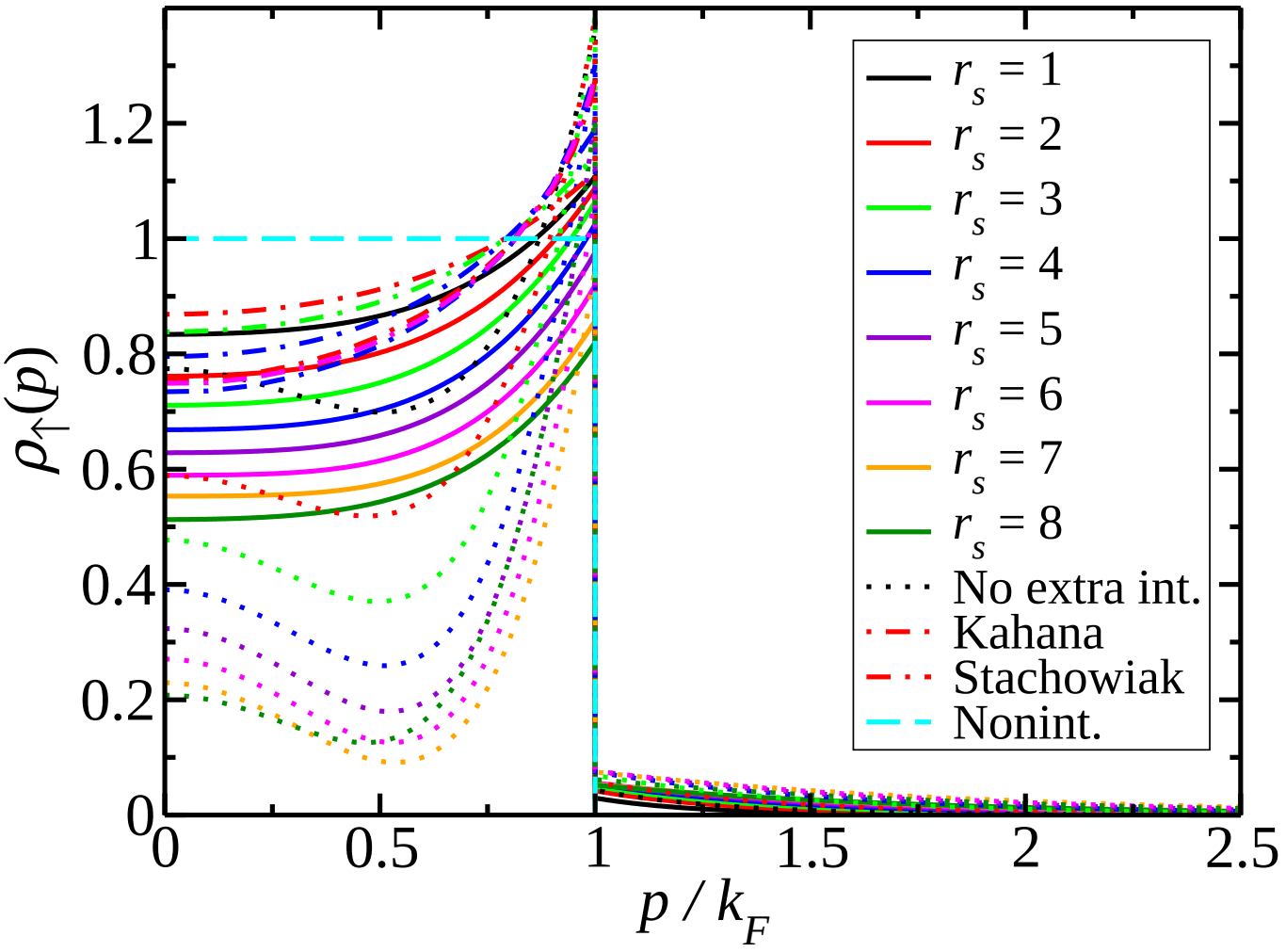
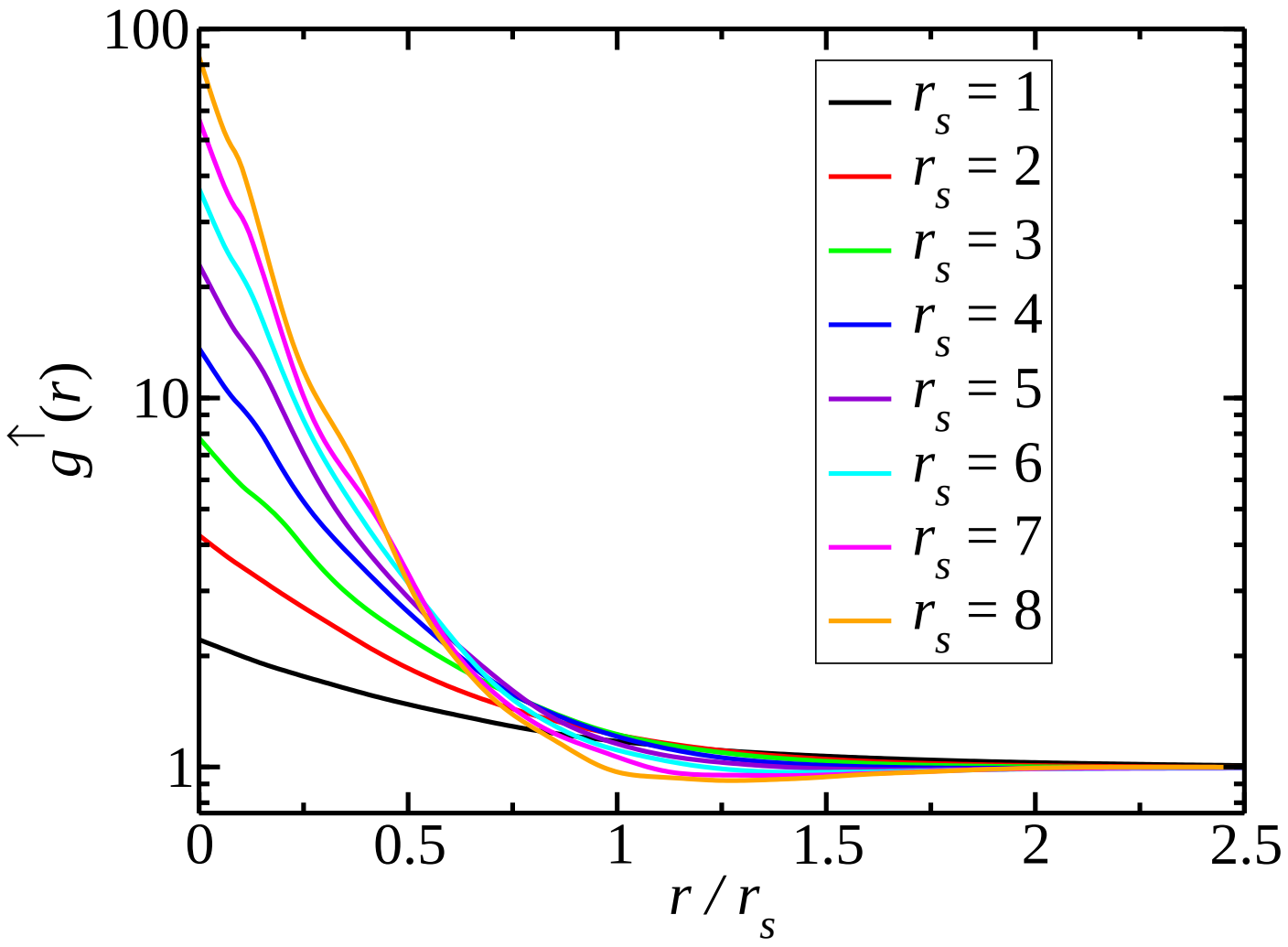
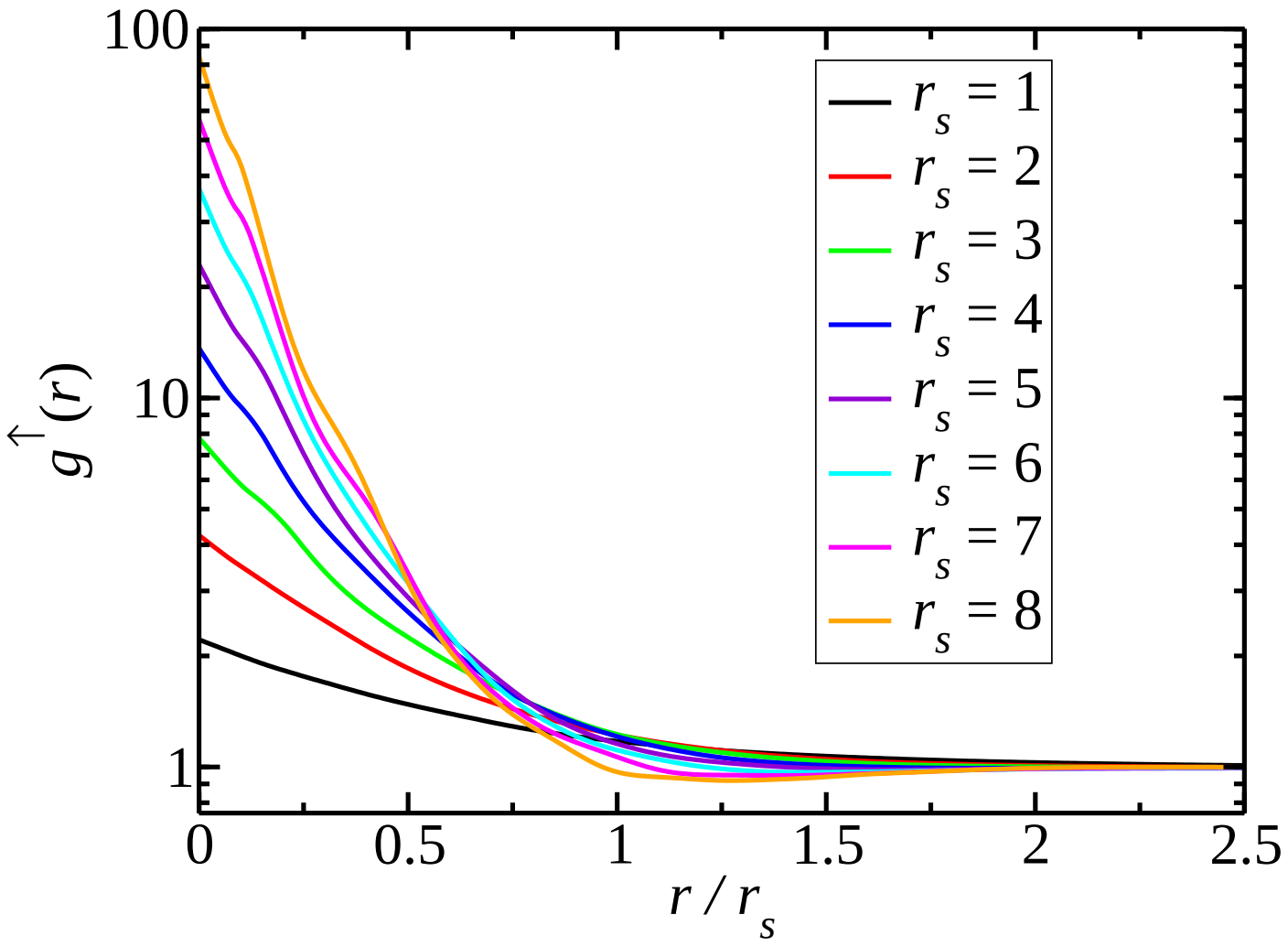


- *The extra interaction is clearly needed when calculating the MD.*
- *Previous results (i) lack the post-edge tail; (ii) disagree with each other and with us.*

Results (III): Pair-Correlation Function



Results (III): Pair-Correlation Function



- *I need to improve the cusp-correction scheme.*

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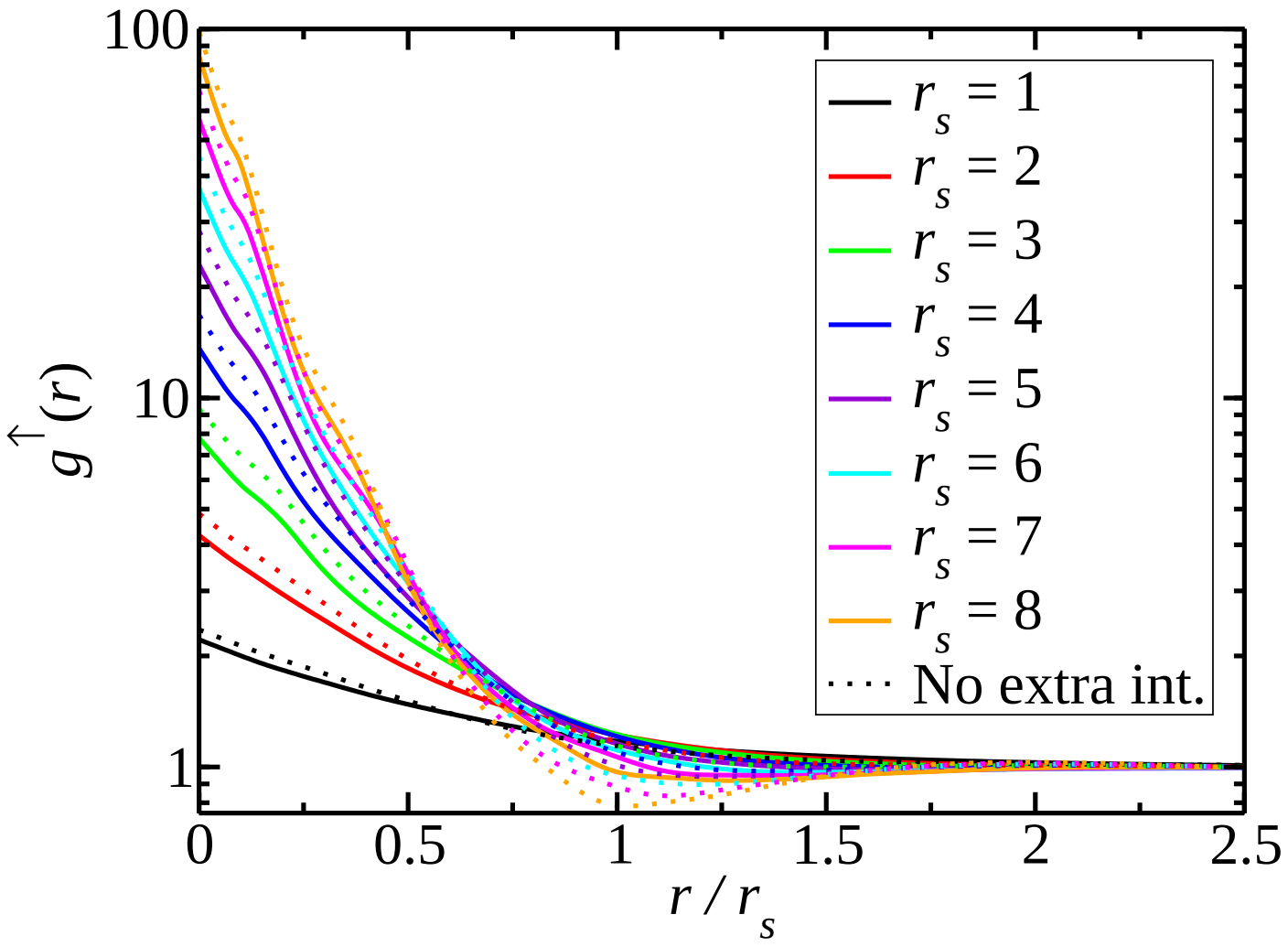

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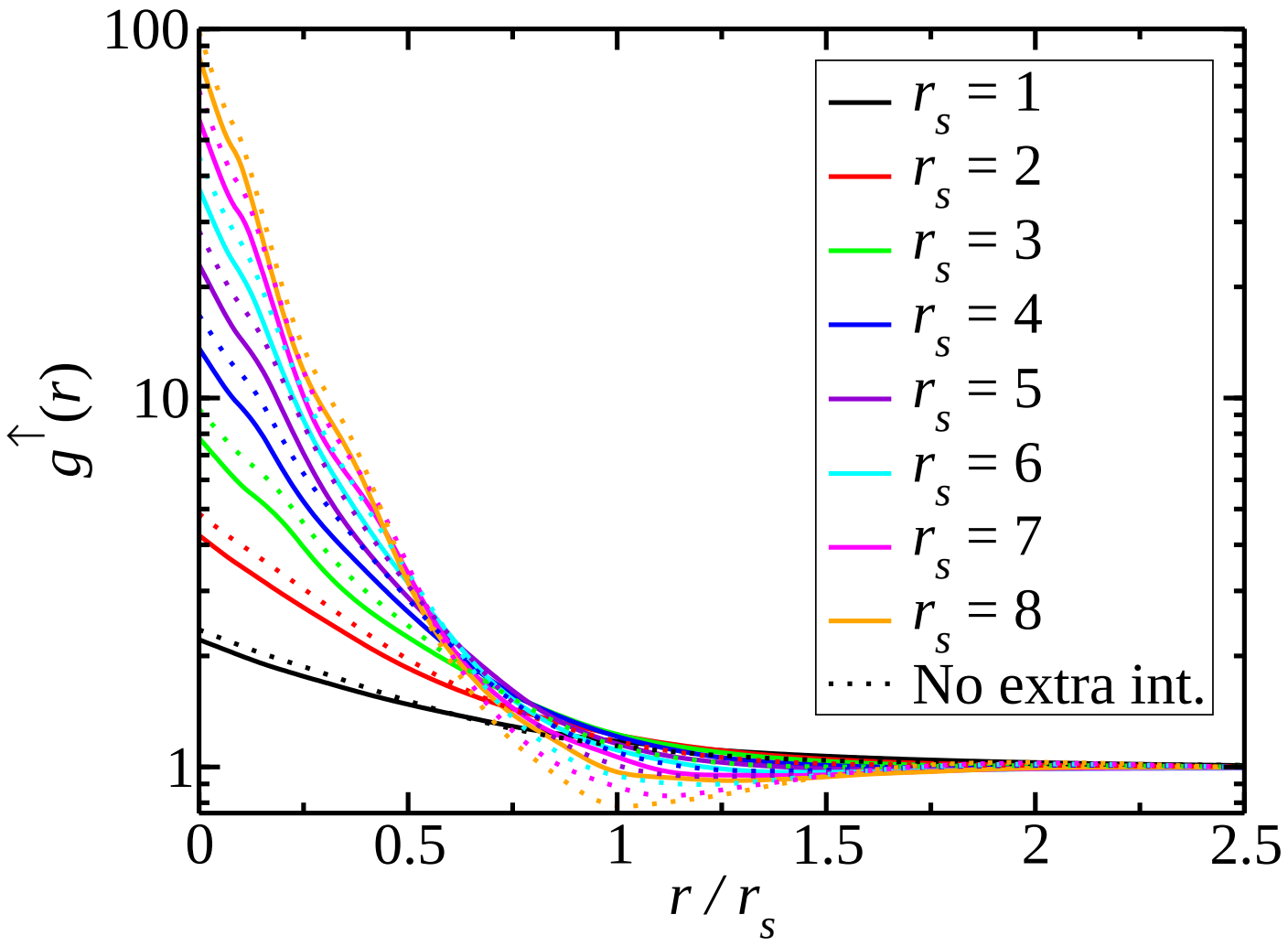
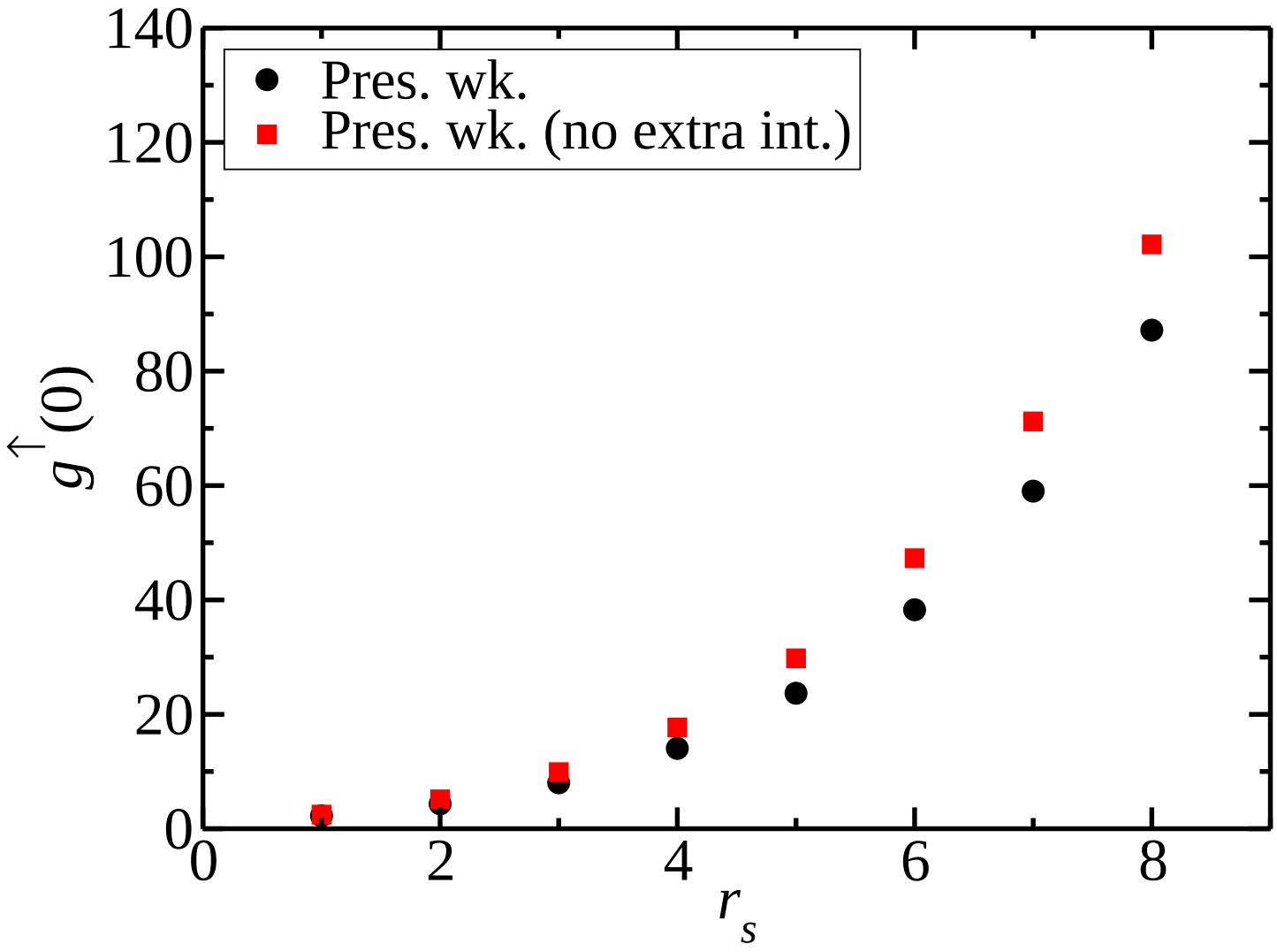
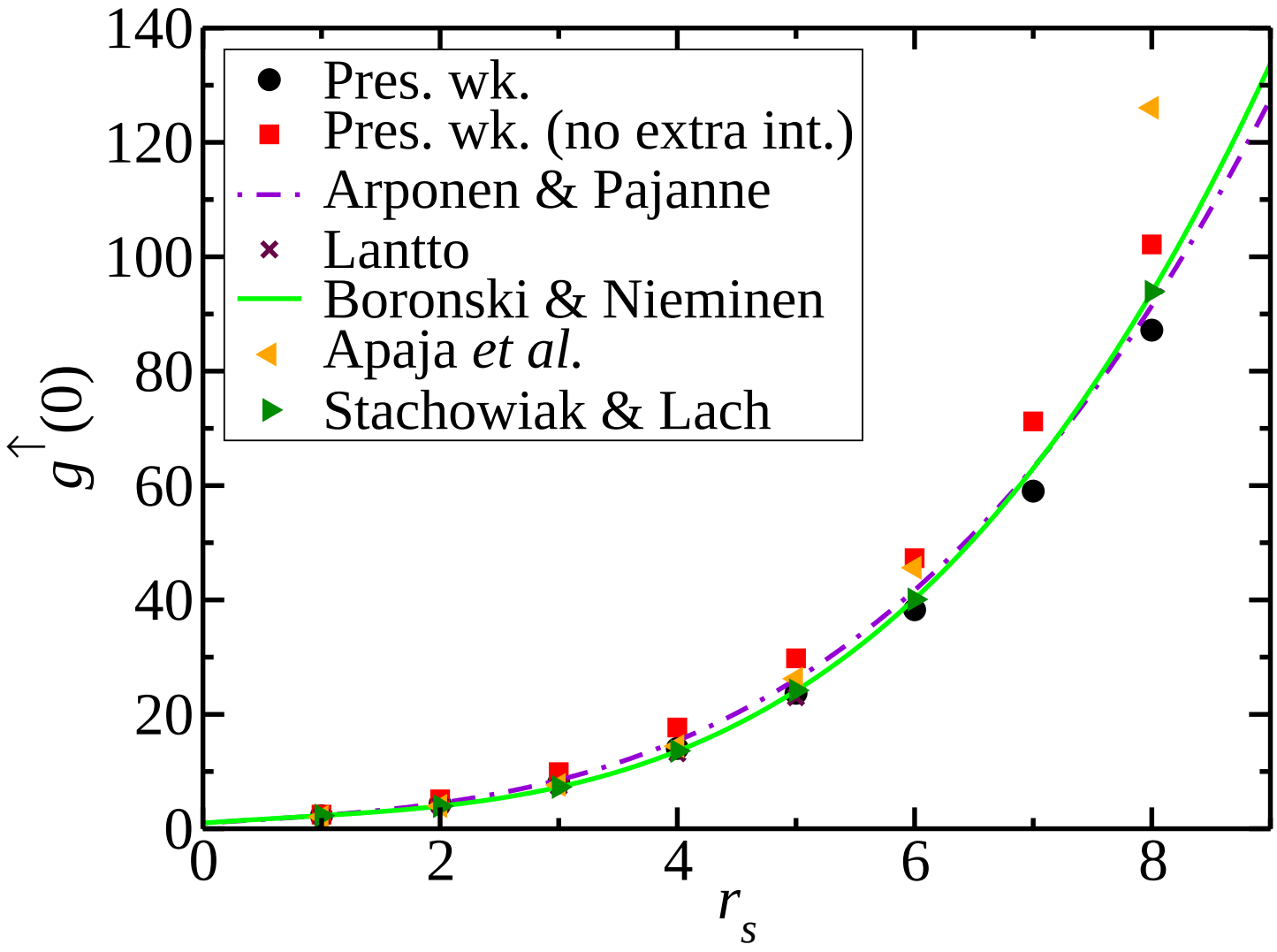


- *I need to improve the cusp-correction scheme.*
- *Extra interaction is important at long range, but not at short range.*

Results (IV): Contact-Density Enhancement Factor



Results (IV): Contact-Density Enhancement Factor



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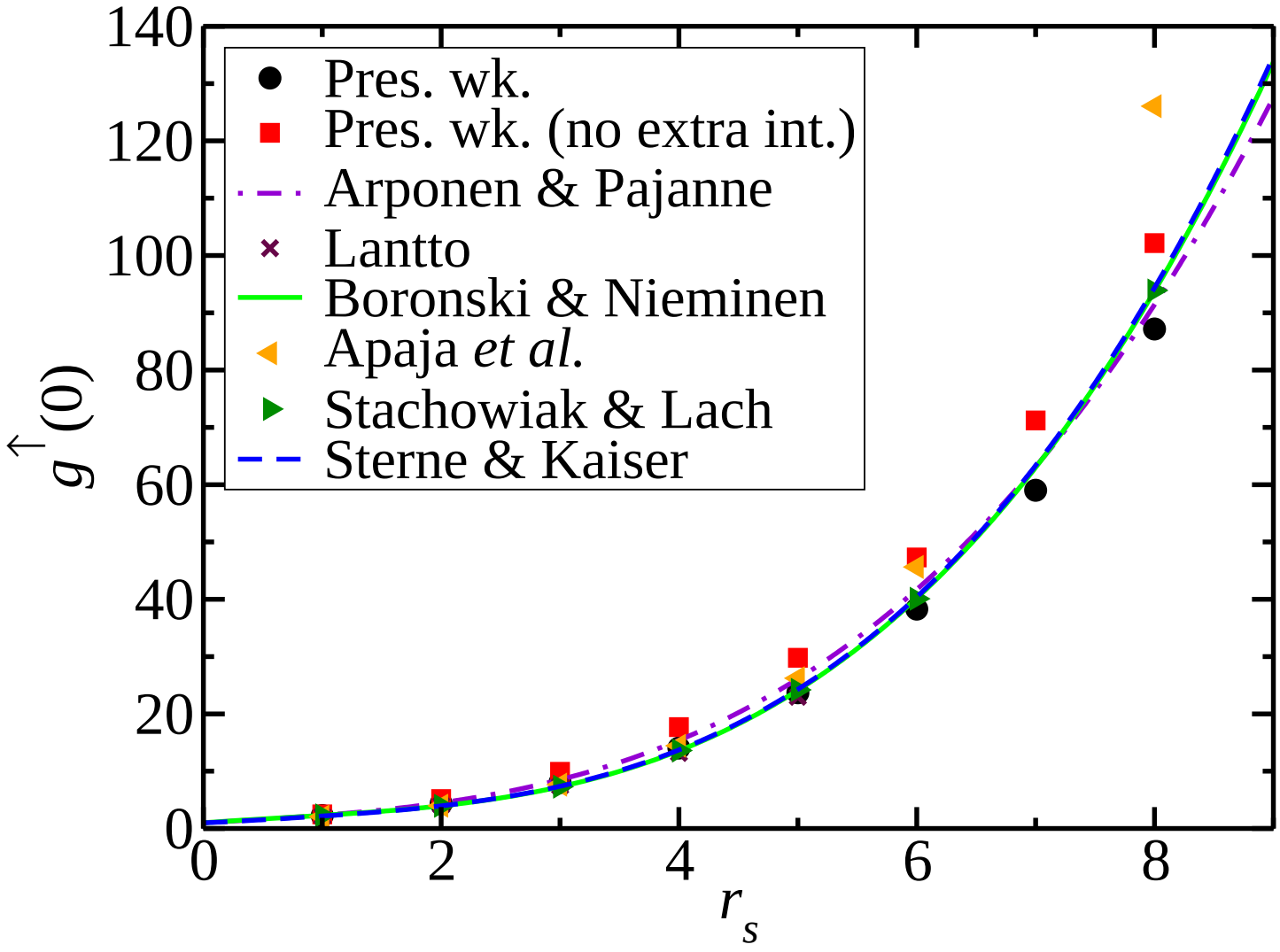

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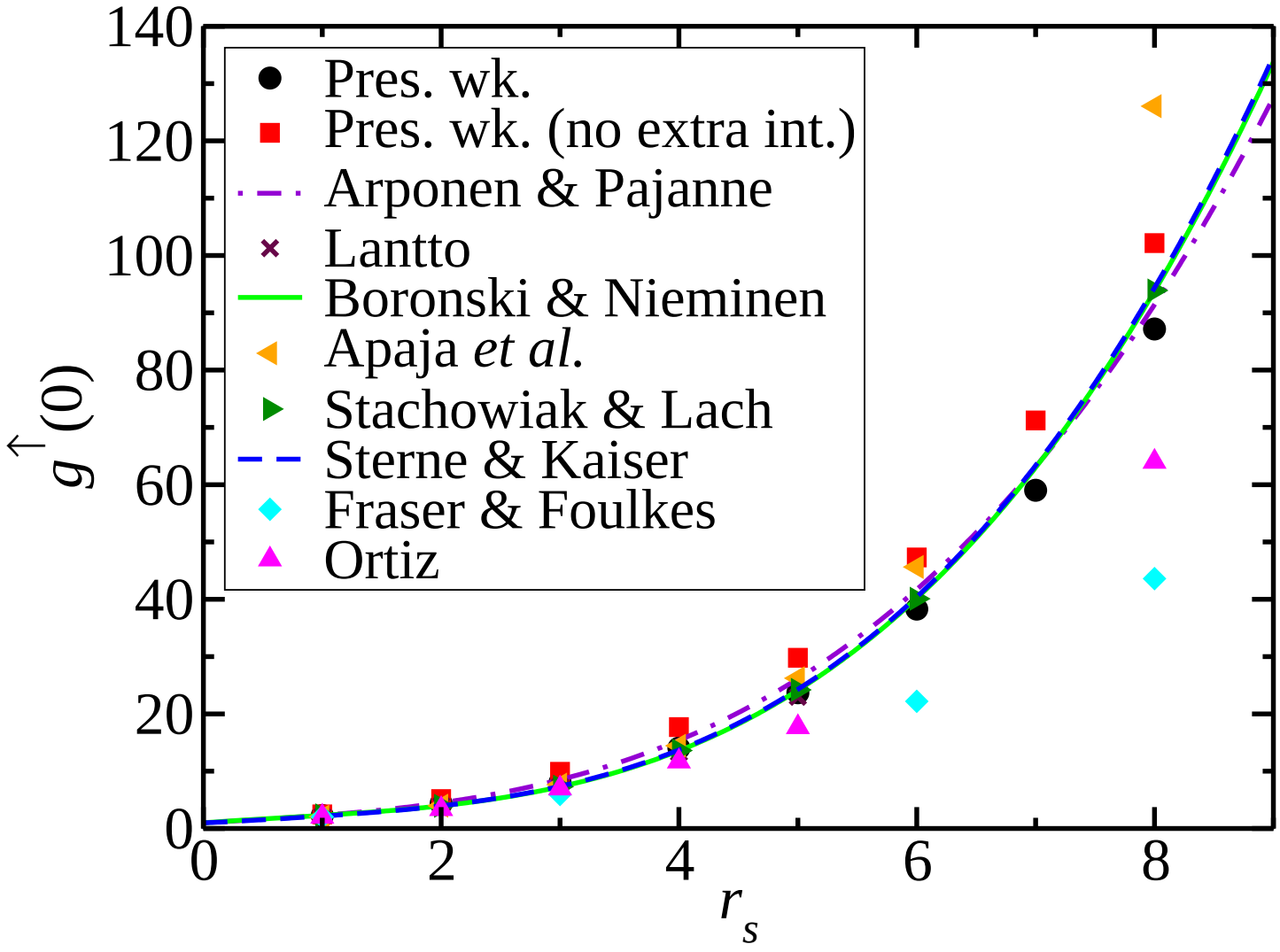

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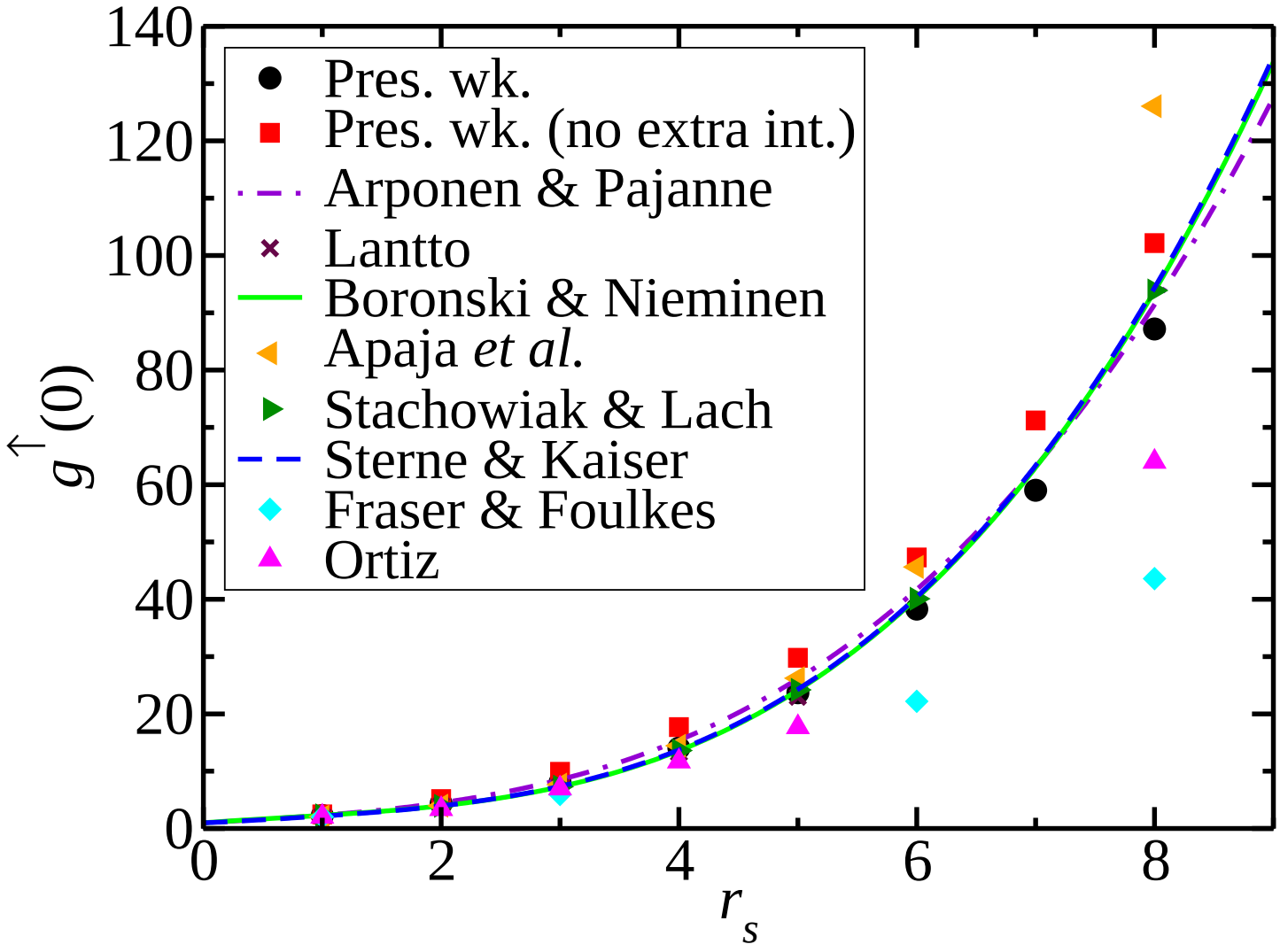

• *Our results are in reasonable agreement with (i) Arponen and Pajanne, (ii) Boroński and Nieminen and (iii) Sterne and Kaiser.*

Quantum Monte Carlo Studies of Positrons in Electron Gases

Previous QMC studies of positrons in HEGs have used plane-wave orbitals for both the electrons and the positron.

But at low densities the positron binds with a single electron to form a positronium atom. *Plane-wave orbitals are therefore completely inappropriate at low density.*

But we can now use pCASTEP to generate pairing orbitals for use in QMC; no difficulty describing positronium. Our DFT results appear to be accurate already; implies that a trial wave function constructed from our orbitals should be very good.

Must either (i) modify the diffusion Monte Carlo Green's function, etc., in accordance with the transformation to the Hamiltonian or (ii) use the electron coordinates relative to the positron in the Slater wave function.

Option (ii) is probably much the easiest way to proceed.

DMC will provide definitive data for the behaviour of positrons in electron gases and pave the way for DFT studies of positrons in real materials, which in turn will extend our abilty to interpret the results of positron-annihilation experiments.

Acknowledgements

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Jesus College
University of Cambridge