Positrons in Homogeneous Electron Gases

Neil D. Drummond*, Chris J. Pickard† and Richard J. Needs*

* **TCM Group, Cavendish Laboratory, University of Cambridge**

† **University of St. Andrews**

QMC in the Apuan Alps II, TTI, Vallico Sotto, Italy

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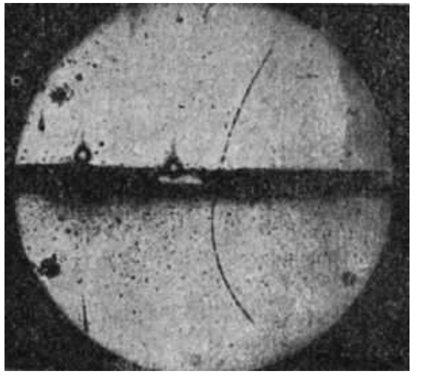
Positrons

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



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

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

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

- Annihilation of a parallel-spin electron-positron pair is a 3rd order process in quantum electrodynamics, producing 3 photons.

- Annihilation of an antiparallel-spin electron-positron pair is a 2nd order process, producing 2 photons.

- We consider only 2-photon annihilation events (experimentally relevant).

- Two-photon annihilation cross-section is $\sigma = \pi/(vc^3)$, where v is the positron velocity and c is the speed of light (in a.u.).[1]

- Positron annihilation is widely used to study material properties. Usual source of positrons in experiments: ${}^{22}_{11}\text{Na}^{11} \rightarrow {}^{22}_{10}\text{Ne}^{12} + \beta^+ + \nu + \gamma$.

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

Positron Lifetime Spectroscopy (POLIS)

- Suppose a positron is injected into a sample of material.

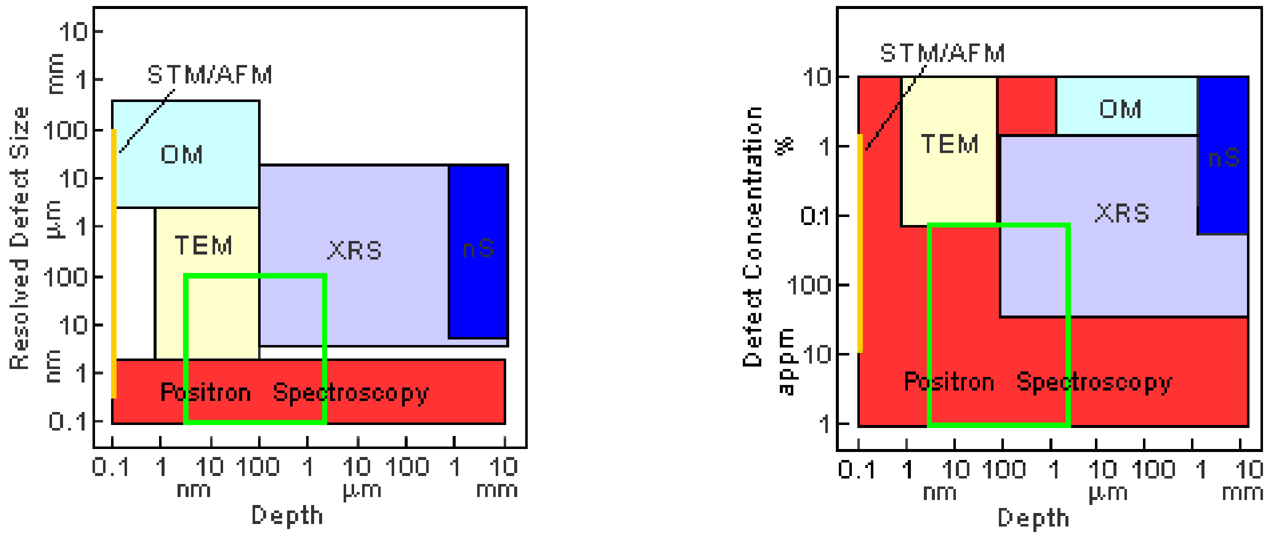
- Positron rapidly thermalises and diffuses through material, before ending up in its ground state. (Often settles in **negatively charged defects**.)

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

- 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.*



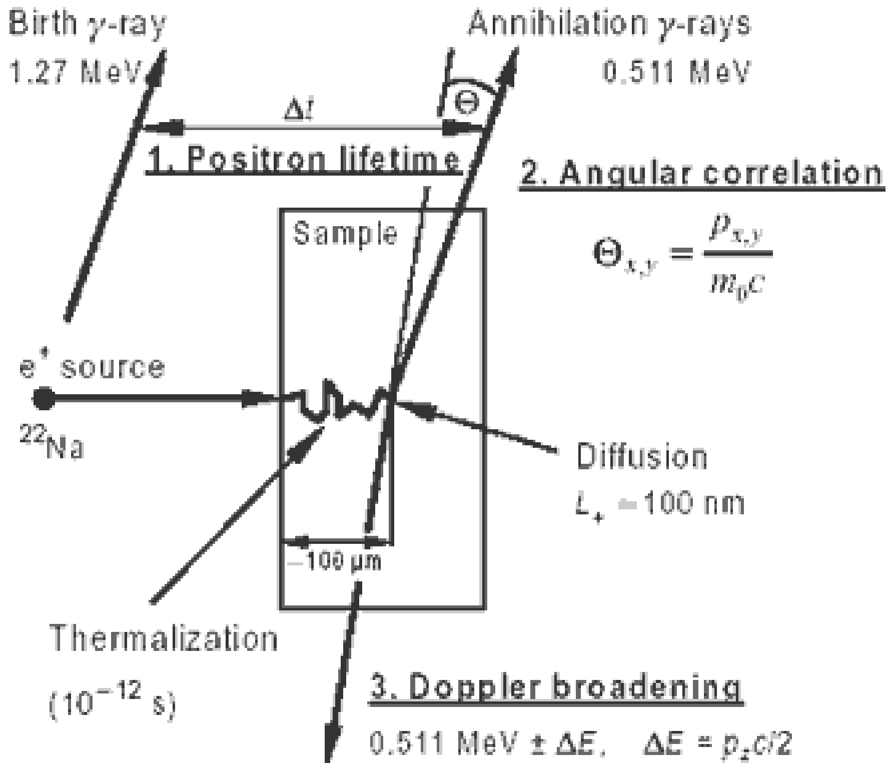
Sensitivity of different experimental methods to defect concentration and size as a function of depth. Green box indicates depth, size and concentration relevent to studies of defects in electronic interconnects on semiconductor chips.

Annihilating-Pair Momentum Spectroscopies

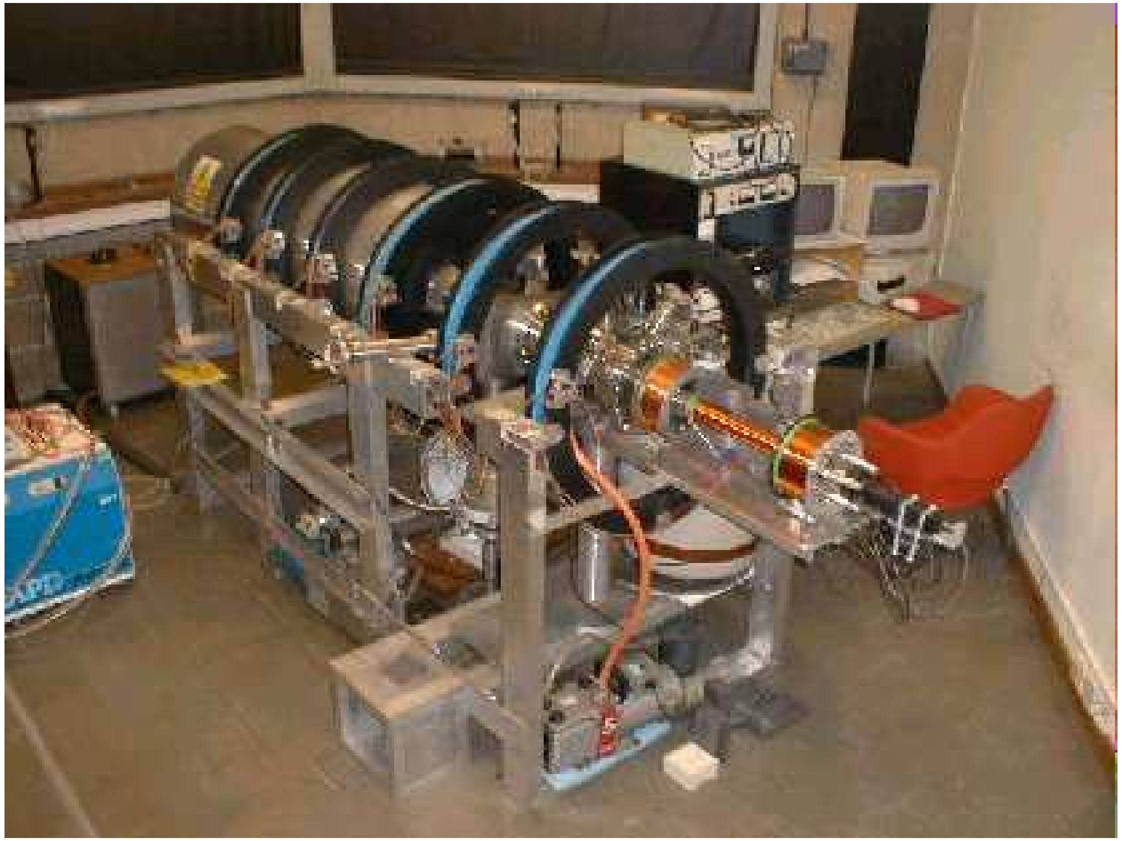
- Conservation of momentum: total momentum of γ rays equals momentum of electron with which positron annihilates.

- Measure distribution of momenta of annihilation radiation to find out distribution of electron momenta.

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



POLIS, DOBS and ACAR spectroscopy.



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:

- 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.

Challenges for Theory

- Positron modifies electron charge density and momentum distribution.

- Annihilation rate by a naïve calculation from cross-section:

$$\lambda = \pi c^{-3} n,$$

  where c is speed of light and n is electron number density.

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

- Positron causes increase in momentum distribution near Fermi edge: *Kahana enhancement*.[2]

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

Positron Immersed in a Homogeneous Electron Gas

- Want to calculate annihilation rates and annihilating-pair momentum distributions for positrons in real materials.

- First step: calculate annihilation rate and momentum distribution for a positron in a homogeneous electron gas.

- Use energy data to construct electron-positron correlation functionals, enabling DFT simulations of positrons in real materials.

Electron-Positron Hamiltonian

- Hamiltonian for positron in homogeneous electron gas:

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

- Make coordinate transformation suggested by Leung *et al.*[3]

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

- Then Hamiltonian is

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

[3] C. H. Leung, *et al.*, Phys. Lett. **57A**, 26 (1976).

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

- Left with Hamiltonian for N interacting particles 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 additional interaction, resembling mass-polarisation. This was neglected by Leung *et al.*, who argued that it is small.

Additional Interaction

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

$$\left\langle \Psi \left| \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \nabla_i \cdot \nabla_j \, \Psi \right. \right\rangle = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \big(\langle \psi_i | \nabla \psi_i \rangle \cdot \langle \psi_j | \nabla \psi_j \rangle - \delta_{m_{s_i}, m_{s_j}} \langle \psi_i | \nabla \psi_j \rangle \cdot \langle \psi_j | \nabla \psi_i \rangle \big),$$

  where m_{s_i} is the spin of particle i.

- First term vanishes in a closed-shell ground state. We consider only closed-shell ground states.

- Require expectation of transformed Hamiltonian to be stationary with respect to variations in each ψ_i; obtain one-electron DFT equations:

$$\left[-\nabla^2 + V_H(\mathbf{x}) + V_{\rm ext}(\mathbf{x}) + V_{\rm xc}(\mathbf{x}) \right] \psi_i(\mathbf{x})$$

$$+\sum_{j=1}^{N} f_j \delta_{m_{s_i}, m_{s_j}} \langle \psi_j | \nabla \psi_i \rangle \cdot \nabla \psi_j(\mathbf{x}) \quad = \quad \epsilon_i \psi_i(\mathbf{x}),$$

where V_H, V_{ext} and V_{xc} are the Hartree, external and exchange-correlation potentials, and f_j and ϵ_j are occupation no. and eigenvalue of state j.

- Equations are solved by a modified version of the CASTEP plane-wave DFT code.[4]

[4] M. D. Segall *et al.*, J. Phys. Cond. Matt. **14**, 2717 (2002).

Positron Pseudopotential

- We use an ultrasoft positron pseudopotential.
- All-electron orbitals recovered using projector augmented-wave method.
- Have checked that results are converged w.r.t. cutoff radius, number of projectors, plane-wave cutoff energy, etc.
- We have used the bare Coulomb potential in some of our calculations.
- Bare Coulomb and pseudopotential calculations are in agreement.

Overlap Integral Theorem for Determinants

Theorem[5]: Let

$$\Psi(\mathbf{R}) = \begin{vmatrix} \psi_1(\mathbf{r}_1) & \cdots & \psi_N(\mathbf{r}_1) \\ \vdots & & \vdots \\ \psi_1(\mathbf{r}_N) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix}$$

and

$$\Phi(\mathbf{R}) = \begin{vmatrix} \phi_1(\mathbf{r}_1) & \cdots & \phi_N(\mathbf{r}_1) \\ \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}.$$

Then

$$\langle \Psi | \Phi \rangle = N! \begin{vmatrix} \langle \psi_1 | \phi_1 \rangle & \cdots & \langle \psi_1 | \phi_N \rangle \\ \vdots & & \vdots \\ \langle \psi_N | \phi_1 \rangle & \cdots & \langle \psi_N | \phi_N \rangle \end{vmatrix}.$$

[5] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).

Annihilating-Pair Momentum Distribution

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

- Positron-electron 1 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 the CoM momentum for positron annihilating with electron 1:

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

- Normalise and use antisymmetry of wave function to get momentum distribution:

$$\rho_{\uparrow}(\bar{\mathbf{p}}) = \frac{\int \cdots \int |\tilde{\Psi}(\bar{\mathbf{p}}, \mathbf{0}; \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N}{\sum_{\bar{\mathbf{p}}} \int \cdots \int |\tilde{\Psi}(\bar{\mathbf{p}}, \mathbf{0}; \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N}$$

$$= \frac{\int \cdots \int \left|\int \exp(-i\bar{\mathbf{p}}\cdot\mathbf{r}_1)\Psi(\mathbf{r}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)\,d\mathbf{r}_1\right|^2\,d\mathbf{r}_2\ldots d\mathbf{r}_N}{V\int\cdots\int|\Psi(\mathbf{r}_1;\mathbf{r}_1,\ldots,\mathbf{r}_N)|^2\,d\mathbf{r}_1\ldots d\mathbf{r}_N}.$$

- Now suppose

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

- Then numerator of momentum distribution is

$$\rho_{\uparrow u}(\bar{\mathbf{p}}) = \frac{1}{N_\uparrow!N_\downarrow!}\int\int \exp\left(i\bar{\mathbf{p}}\cdot(\mathbf{r}_1'-\mathbf{r}_1)\right)$$

$$
\begin{aligned}
\times \quad & \int \cdots \int \begin{vmatrix} \phi_1^{\uparrow *}(\mathbf{0}) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{0}) \\ \phi_1^{\uparrow *}(\mathbf{r_2}'' - \mathbf{r}'_1) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{r}''_2 - \mathbf{r}'_1) \\ \vdots & & \vdots \\ \phi_1^{\uparrow *}(\mathbf{r}''_{N_\uparrow} - \mathbf{r}'_1) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{r}''_{N_\uparrow} - \mathbf{r}'_1) \end{vmatrix} \\
& \times \begin{vmatrix} \phi_1^{\uparrow}(\mathbf{0}) & \cdots & \phi_{N_\uparrow}^{\uparrow}(\mathbf{0}) \\ \phi_1^{\uparrow}(\mathbf{r_2}'' - \mathbf{r}_1) & \cdots & \phi_{N_\uparrow}^{\uparrow}(\mathbf{r}''_2 - \mathbf{r}_1) \\ \vdots & & \vdots \\ \phi_1^{\uparrow}(\mathbf{r}''_{N_\uparrow} - \mathbf{r}_1) & \cdots & \phi_{N_\uparrow}^{\uparrow}(\mathbf{r}''_{N_\uparrow} - \mathbf{r}_1) \end{vmatrix} d\mathbf{r}''_2 \ldots d\mathbf{r}''_{N_\uparrow} \\
& \times \int \cdots \int \begin{vmatrix} \phi_1^{\downarrow *}(\mathbf{r}''_{N_\uparrow+1} - \mathbf{r}'_1) & \cdots & \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r}''_{N_\uparrow+1} - \mathbf{r}'_1) \\ \vdots & & \vdots \\ \phi_1^{\downarrow *}(\mathbf{r}''_N - \mathbf{r}'_1) & \cdots & \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r}''_N - \mathbf{r}'_1) \end{vmatrix} \\
& \times \begin{vmatrix} \phi_1^{\downarrow}(\mathbf{r}''_{N_\uparrow+1} - \mathbf{r}_1) & \cdots & \phi_{N_\downarrow}^{\downarrow}(\mathbf{r}''_{N_\uparrow+1} - \mathbf{r}_1) \\ \vdots & & \vdots \\ \phi_1^{\downarrow}(\mathbf{r}''_N - \mathbf{r}_1) & \cdots & \phi_{N_\downarrow}^{\downarrow}(\mathbf{r}''_N - \mathbf{r}_1) \end{vmatrix} d\mathbf{r}''_{N_\uparrow+1} \ldots d\mathbf{r}''_N \, d\mathbf{r}'_1 \, d\mathbf{r}_1
\end{aligned}
$$

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

- We have: (i) substituted $\mathbf{R} = \mathbf{r}_1 - \mathbf{r}_1'$; (ii) substituted $\mathbf{r}_i = \mathbf{r}_i'' - \mathbf{r}_1'$ $\forall i \in \{2, \ldots, N\}$, allowing us to perform the integral over $\mathbf{r}_1'$; (iii) made use of the overlap integral theorem; (iv) defined M_{ij} to be the (i, j)th minor of

$$
\begin{vmatrix} \phi_1^{\uparrow *}(\mathbf{0}) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{0}) \\ \phi_1^{\uparrow *}(\mathbf{r_2}) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{r}_2) \\ \vdots & & \vdots \\ \phi_1^{\uparrow *}(\mathbf{r}_{N_\uparrow}) & \cdots & \phi_{N_\uparrow}^{\uparrow *}(\mathbf{r}_{N_\uparrow}) \end{vmatrix};
$$

and (v) defined N_{ij} to be the (i, j)th minor of

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

- 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 distribution is

$$\rho_{\uparrow u}(\bar{\mathbf{p}}) \quad = \quad \int \exp(-i\bar{\mathbf{p}} \cdot \mathbf{R}) \sum_{i=1}^{N_\uparrow} \sum_{j=1}^{N_\uparrow} (-1)^{i+j} \phi_i^{\uparrow *}(\mathbf{0}) \phi_j^{\uparrow}(\mathbf{0}) \det\left(B^{\mathbf{R}}(i,j)\right)$$

$$\times \begin{vmatrix} \int \phi_1^{\downarrow *}(\mathbf{r})\phi_1^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} & \cdots & \int \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r})\phi_1^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} \\ \vdots & & \vdots \\ \int \phi_1^{\downarrow *}(\mathbf{r})\phi_{N_\downarrow}^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} & \cdots & \int \phi_{N_\downarrow}^{\downarrow *}(\mathbf{r})\phi_{N_\downarrow}^{\downarrow}(\mathbf{r}-\mathbf{R})\, d\mathbf{r} \end{vmatrix} d\mathbf{R}.$$

Electron-Positron Pair-Correlation Function

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

$$g^{\uparrow}(\mathbf{r},\mathbf{s}) = \frac{\rho_{1p}^{\uparrow}(\mathbf{r},\mathbf{s})}{\rho_1^{\uparrow}(\mathbf{r})\rho_p(\mathbf{s})} = V^2 \frac{\int \cdots \int |\Psi(\mathbf{s};\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N)|^2 \, d\mathbf{r}_2 \ldots d\mathbf{r}_N}{\int \cdots \int \int |\Psi(\mathbf{s};\mathbf{r}_1,\ldots,\mathbf{r}_N)|^2 \, d\mathbf{r}_1 \ldots d\mathbf{r}_N \, d\mathbf{s}}.$$

- Denominator:

$$V \begin{vmatrix} \langle \phi_1^{\uparrow} | \phi_1^{\uparrow} \rangle & \cdots & \langle \phi_1^{\uparrow} | \phi_{N_\uparrow}^{\uparrow} \rangle \\ \vdots & & \vdots \\ \langle \phi_{N_\uparrow}^{\uparrow} | \phi_1^{\uparrow} \rangle & \cdots & \langle \phi_{N_\uparrow}^{\uparrow} | \phi_{N_\uparrow}^{\uparrow} \rangle \end{vmatrix} \times \begin{vmatrix} \langle \phi_1^{\downarrow} | \phi_1^{\downarrow} \rangle & \cdots & \langle \phi_1^{\downarrow} | \phi_{N_\downarrow}^{\downarrow} \rangle \\ \vdots & & \vdots \\ \langle \phi_{N_\downarrow}^{\downarrow} | \phi_1^{\downarrow} \rangle & \cdots & \langle \phi_{N_\downarrow}^{\downarrow} | \phi_{N_\downarrow}^{\downarrow} \rangle \end{vmatrix}.$$

- Numerator:

$$\frac{V^2}{N_\uparrow!}\int\cdots\int\left\|\begin{array}{ccc}\phi_1^\uparrow(\mathbf{r}-\mathbf{s}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}-\mathbf{s})\\ \phi_1^\uparrow(\mathbf{r}_2) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_2)\\ \vdots & & \vdots\\ \phi_1^\uparrow(\mathbf{r}_{N_\uparrow}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_{N_\uparrow})\end{array}\right\|^2 d\mathbf{r}_2\ldots d\mathbf{r}_{N_\uparrow}$$

$$\times\left|\begin{array}{ccc}\langle\phi_1^\downarrow|\phi_1^\downarrow\rangle & \cdots & \langle\phi_1^\downarrow|\phi_{N_\downarrow}^\downarrow\rangle\\ \vdots & & \vdots\\ \langle\phi_{N_\downarrow}^\downarrow|\phi_1^\downarrow\rangle & \cdots & \langle\phi_{N_\downarrow}^\downarrow|\phi_{N_\downarrow}^\downarrow\rangle\end{array}\right|.$$

- But

$$\int\cdots\int\left\|\begin{array}{ccc}\phi_1^\uparrow(\mathbf{r}-\mathbf{s}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}-\mathbf{s})\\ \phi_1^\uparrow(\mathbf{r}_2) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_2)\\ \vdots & & \vdots\\ \phi_1^\uparrow(\mathbf{r}_{N_\uparrow}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_{N_\uparrow})\end{array}\right\|^2 d\mathbf{r}_2\ldots d\mathbf{r}_{N_\uparrow}$$

$$= \sum_{i=1}^{N_\uparrow} \sum_{j=1}^{N_\uparrow} (-1)^{i+j} \phi_i^{\uparrow *}(\mathbf{r}-\mathbf{s}) \phi_j^{\uparrow}(\mathbf{r}-\mathbf{s}) \int \cdots \int N_{1i}^* N_{1j} \, d\mathbf{r}_2 \ldots d\mathbf{r}_N$$

$$= (N_\uparrow - 1)! \sum_{i=1}^{N_\uparrow} \sum_{j=1}^{N_\uparrow} (-1)^{i+j} \phi_i^{\uparrow *}(\mathbf{r}-\mathbf{s}) \phi_j^{\uparrow}(\mathbf{r}-\mathbf{s}) \det(B(i,j)),$$

where N_{ij} is the (i,j)th minor of

$$\begin{vmatrix} \phi_1^\uparrow(\mathbf{r}-\mathbf{s}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}-\mathbf{s}) \\ \phi_1^\uparrow(\mathbf{r}_2) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_2) \\ \vdots & & \vdots \\ \phi_1^\uparrow(\mathbf{r}_{N_\uparrow}) & \cdots & \phi_{N_\uparrow}^\uparrow(\mathbf{r}_{N_\uparrow}) \end{vmatrix}$$

and the overlap integral theorem is used to define the matrix $B(i,j)$ for each i and j.

- So

$$g^{\uparrow}(\mathbf{r}-\mathbf{s}) = \frac{V\sum_{i=1}^{N_\uparrow}\sum_{j=1}^{N_\uparrow}(-1)^{i+j}\phi_i^{\uparrow *}(\mathbf{r}-\mathbf{s})\phi_j^{\uparrow}(\mathbf{r}-\mathbf{s})\det(B(i,j))}{N_\uparrow \begin{vmatrix} \langle\phi_1^\uparrow|\phi_1^\uparrow\rangle & \cdots & \langle\phi_1^\uparrow|\phi_{N_\uparrow}^\uparrow\rangle \\ \vdots & & \vdots \\ \langle\phi_{N_\uparrow}^\uparrow|\phi_1^\uparrow\rangle & \cdots & \langle\phi_{N_\uparrow}^\uparrow|\phi_{N_\uparrow}^\uparrow\rangle \end{vmatrix}}.$$

- Have written a code to evaluate the momentum distribution and PCF.

- NB, augmented orbitals (pseudo-orbitals in plane waves plus augmentation functions on radial grid) must be used.

Contact Density Enhancement and Annihilation Rate

- Probability density that a spin-up electron coincides with 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:

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

Immersion and Relaxation Energies

- Let $E(N, M, V)$ be the energy of a uniform plasma of N electrons and M positrons in fixed volume V.

- *Immersion energy* of a positron:

$$\Delta E \equiv E(N+1,1,V) - E(N,0,V) - E(1,1,V).$$

- *Relaxation energy* of a positron:

$$\begin{aligned}\Delta\Omega &\equiv E(N+1,1,V) - E(N+1,0,V) \\ &= \Delta E + E(N,0,V) - E(N+1,0,V) + E(1,1,V) \\ &= \Delta E - \mu(N,V) + E(1,1,V) + \mathcal{O}(N^{-1}),\end{aligned}$$

where

$$\mu(N,V) \equiv \left(\frac{\partial E}{\partial N}\right)_{N,0,V}$$

is the zero-temperature chemical potential of the N-electron HEG.

- In the infinite-system limit,

$$\Delta\Omega(r_s) = \Delta E(r_s) - \mu(r_s) + E_{\rm pos},$$

- Zero-temperature chemical potential of a HEG is given by

$$\mu = \frac{d}{dn}(n\mathcal{E}) = \mathcal{E} - \frac{1}{3} r_s \frac{d\mathcal{E}}{dr_s},$$

  where n is number density and $\mathcal{E}$ is total energy per electron.

- Chemical potential is easily calculated within HF theory.

- Correlation chemical potential has been parametrised by Perdew and Zunger[6] (using Gell-Mann & Brueckner's analytical result for high-density HEG and Ceperley-Alder DMC data for $r_s \geq 1$).

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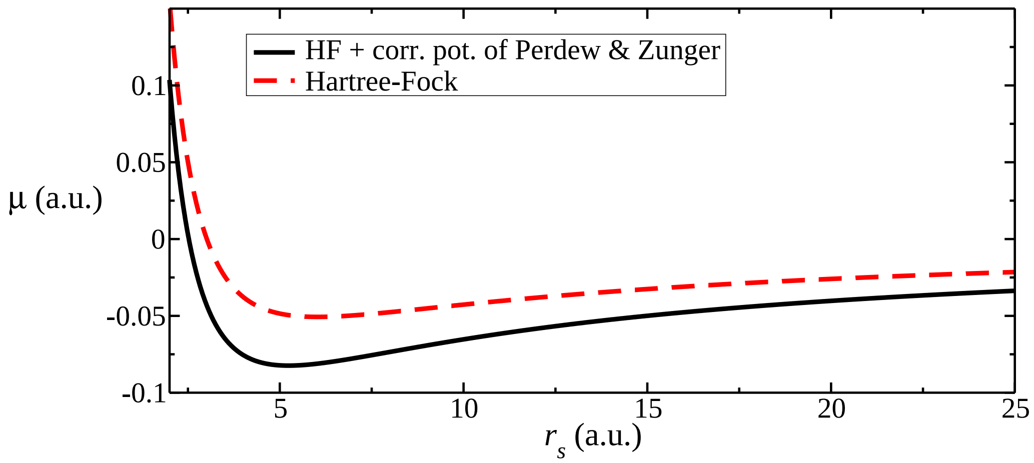
[6] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).



- *Hence we can obtain the immersion energy from relaxation-energy calculations and* vice versa.

Electron-Positron Correlation Functionals

- If there is no electron-positron correlation then the positron occupies its zero-momentum ground state.

- In this case, energy of the HEG+positron is same as energy of the HEG.

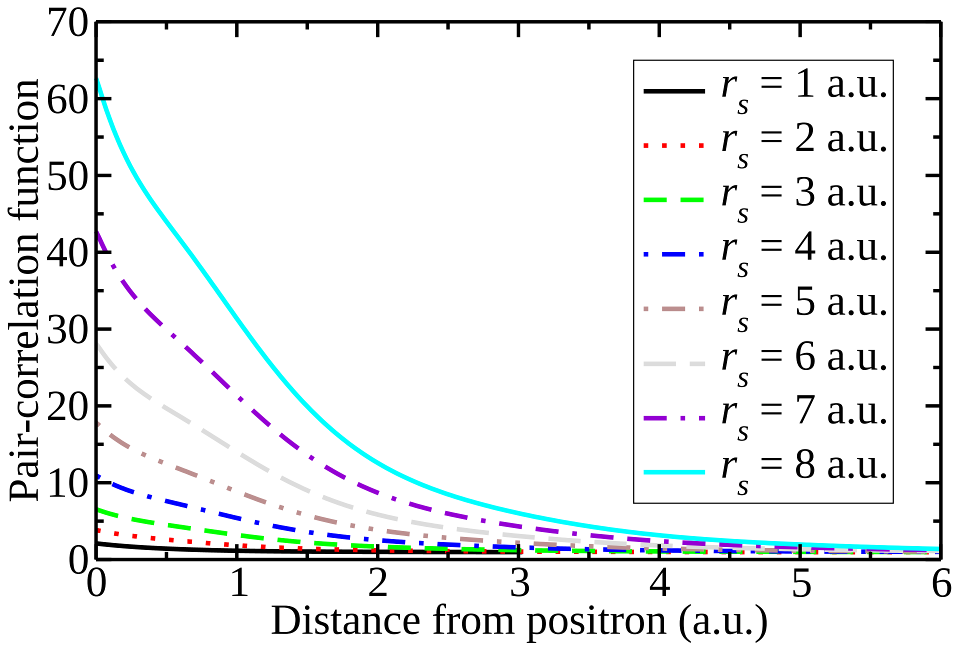
- So the electron-positron correlation energy is the difference of the energy of the HEG+positron and the HEG.

- This is just the relaxation energy; can calculate it as a function of r_s.

- Hence we can construct an electron-positron correlation functional, for use in DFT studies of positrons in real materials.

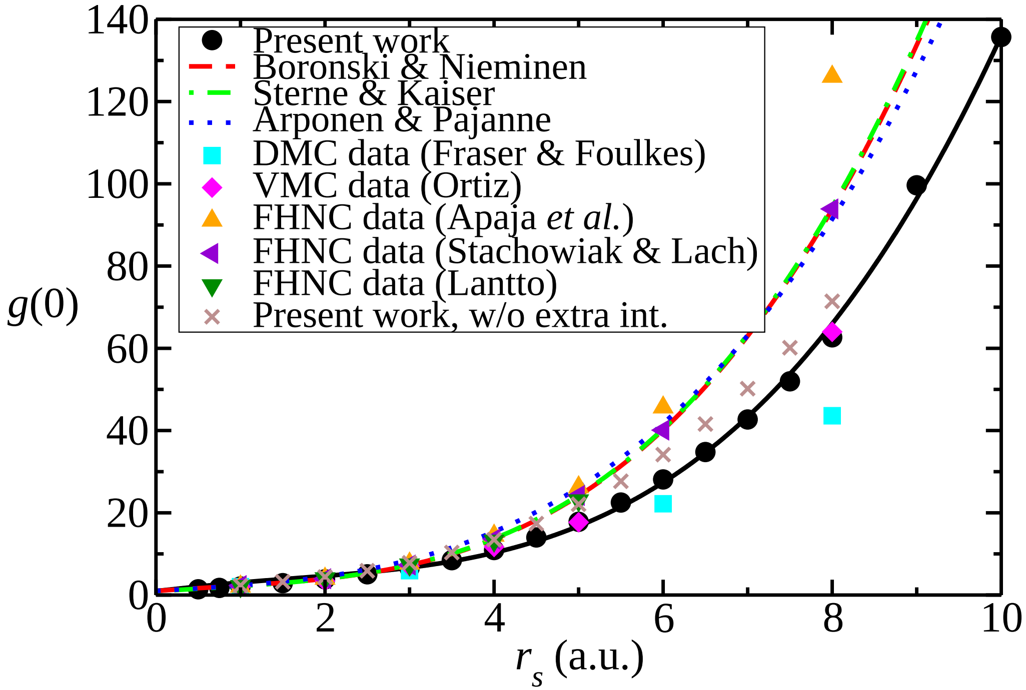
Preliminary results

Pair correlation function



Contact PCF is of greatest interest.

Contact density enhancement factor[7]



- Our results agree with the VMC calculations of Ortiz.
- Extra interaction is important, especially at high densities.

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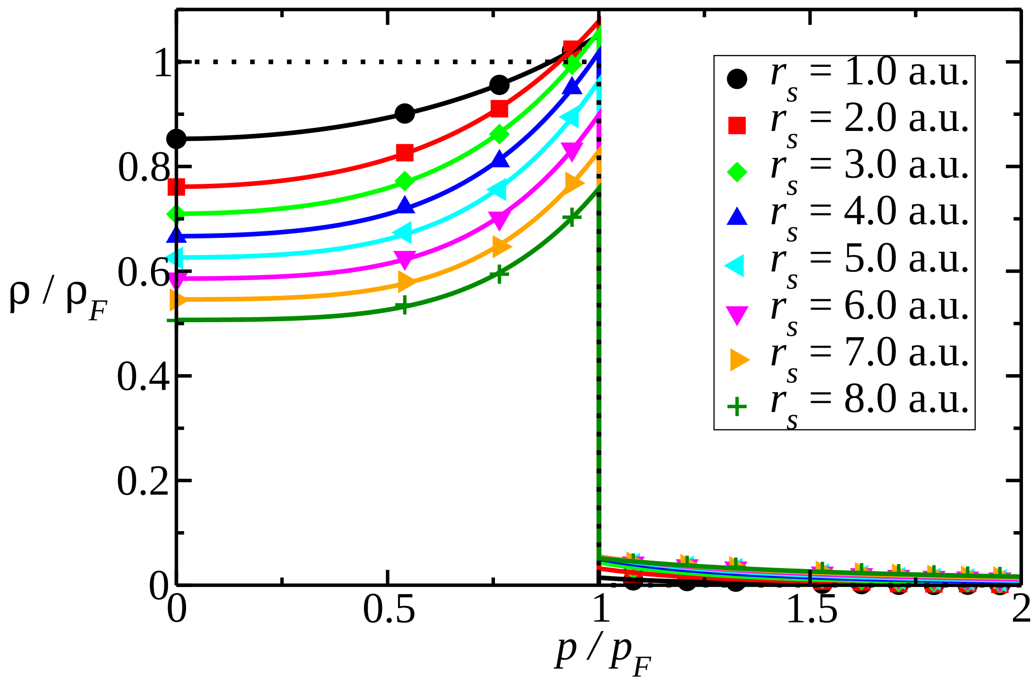
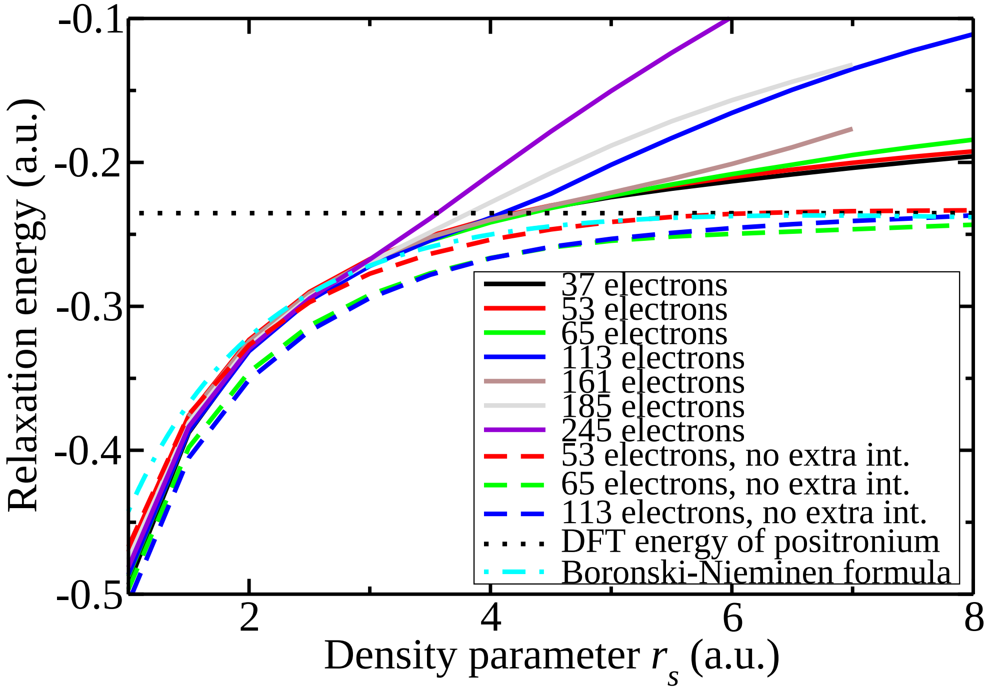
[7] P. A. Sterne & J. H. Kaiser, Phys. Rev. B **43**, 13892 (1991); E. Boroński & R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986); J. Arponen & E. Pajanne, J. Phys. F **9**, 2359 (1979); G. Ortiz, PhD thesis, Lausanne (1992); L. Fraser, PhD thesis, London (1995); V. Apaja *et al.*, Phys. Rev. B **68**, 195118 (2003); H. Stachowiak & J. Lach, Phys. Rev. B **48**, 9828 (1993); L. J. Lantto, Phys. Rev. B **36**, 5160 (1987).

Annihilating-pair momentum distribution



Maximum Kahana enhancement at $r_s \approx 2$ a.u.

Relaxation energy[8]



- Well behaved for small systems, badly behaved for large ones.
- *Perhaps CASTEP is converging to the wrong self-consistent solution?*

[8] E. Boroński & R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986)

QMC Studies of Positrons in Electron Gases

- Previous QMC studies of positrons in HEGs have used plane-wave orbitals for the electrons and positron.
- At low densities positron binds with a single electron to form a positronium atom.
- Plane-wave orbitals are inappropriate for describing positronium.
- We can use modified CASTEP to generate orbitals for CASINO; no difficulty describing positronium.
- Will either have to (i) modify DMC 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 the easiest way to proceed.
- **DMC should be able to provide definitive answers to these technologically important questions about the behaviour of positrons in materials.**

Acknowledgements

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