Gradient correction scheme for bulk and defect positron states in materials: New developments

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In general

- The positron lifetime (τ) and affinity (A_+) are fundamental positron characteristics.
- They are often used to interpret experimental data in positron defect studies.
- But even more importantly τ and A_+ are properties which reflect fundamental interactions – electron-electron and electron-positron – in solids.
- Comparing experimental and theoretical counterparts may teach us about the validity of our theory, but it may also doubt an interpretation of our experiment in some cases.
- Studying electron-electron and electron-positron interactions is not easy because all particles strongly interact.
- But the efforts certainly pay off when a deeper understanding is achieved.

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Basic ideas

- The two-component density functional theory says that the ground state total energy of a system composed of electrons and positrons (and nuclei) is a functional of the electron (ρ^-) and positron (ρ^+) density ($E \equiv E[\rho^-, \rho^+]$).
- The local density approximation (LDA) means that the exchange-correlation part of the $E[\rho^-, \rho^+]$ functional is constructed using the quantities coming from theories of the homogeneous electron gas.
- In the case of generalized gradient approximation (GGA) this exchange-correlation term depends also on the gradient of the electron density ($\nabla\rho^-$).

Enhancement details

- In the GGA for electrons one can define a dimensionless parameter

$$\epsilon = \frac{|\nabla \rho^-|^2}{(\rho^- q_{TF})^2} = \frac{\pi |\nabla \rho^-|^2}{4(\rho^-)^2 (3\pi^2 \rho^-)^{\frac{1}{3}}}$$

  with $1/q_{TF}$ being the local Thomas-Fermi screening length; $q_{TF}^2 = 4(3\pi^2\rho^-)^{\frac{1}{3}}\ \pi$.

- Then, we postulate that the electron screening cloud around positron within GGA is reduced with respect to the LDA screening cloud by an exponential factor

$$\Delta\bar{\rho}_{GGA} = \Delta\bar{\rho}_{LDA}\ \exp\left(-\alpha\epsilon\right)$$

  where $\alpha > 0$ is an empirical parameter to be determined by comparison with experiment.

Enhancement details

- Since the screening charge in LDA is in fact given by the enhancement factor (contact density) as $\gamma_{LDA} - 1$, we can define the GGA enhancement factor as follows

$$\gamma_{GGA} = 1 + (\gamma_{LDA} - 1) \exp(-\alpha\epsilon) .$$

- In the original approach by Barbiellini et al. [PRB **51**, 7341 (1995)], $\alpha = 0.22$ using the LDA enhancement after Arponen and Pajanne:

$$\gamma_{LDA} = 1 + 1.23 r_s - 0.0742 r_s^2 + r_s^3/6 .$$

- Recently, Boroński [Nukleonika **55**, 9 (2010)] suggested to use perturbed hypernetted chain result [Stachowiak and Lach, PRB **48**, 9828 (1993)]

$$\gamma_{LDA} = 1 + 1.23 r_s - 0.1375 r_s^2 + r_s^3/6$$

with $\alpha = 0.10$.

Enhancement details

- Very recently Drummond et al. [PRL **107**, 207402 (2011)] on the basis of quantum Monte Carlo determined another LDA enhancement which reads

$$\begin{aligned}\gamma_{LDA} &= 1 + 1.23 r_s - 3.38208 r_s^{3/2} + 8.6957 r_s^2 - \\ &- 7.37037 r_s^{7/3} + 1.75648 r_s^{8/3} + 0.173694 r_s^3 \,.\end{aligned}$$

  In this case, we suggest to use $\alpha = 0.05$ for the positron GGA.

- For the purpose of testing, we also use the original enhancement of Boroński and Nieminen [PRB **34**, 3820 (1986)]

$$\gamma_{LDA} = 1 + 1.23 r_s + 0.8295 r_s^{3/2} - 1.26 r_s^2 + 0.3286 r_s^{5/2} + r_s^3/6 \,.$$

Positron treatment details

- The positron ground state wave function is obtained by solving the Schrödinger equation

$$\left[-\frac{1}{2}\nabla_{\boldsymbol{r}}^2 - V^c(\boldsymbol{r}) + V^{ep}(\boldsymbol{r})\right]\psi^+(\boldsymbol{r}) = E^+\psi^+(\boldsymbol{r})\,.$$

- In the case of the positron correlation potential, the GGA is applied as follows

$$V^{ep}_{GGA} = V^{ep}_{LDA}\exp(-\alpha\epsilon/3)\,.$$

- The positron lifetime (τ) is calculated via the positron annihilation rate (λ) according to the formula

$$\frac{1}{\tau} = \lambda = \pi r_0^2 c \int \mathrm{d}\boldsymbol{r}\,\rho^+(\boldsymbol{r})\,\rho^-(\boldsymbol{r})\,\gamma[\rho^-(\boldsymbol{r}),\epsilon(\boldsymbol{r})] = \int \mathrm{d}\boldsymbol{r}\,\lambda_i(\boldsymbol{r})\,.$$

  considering that $\rho^+ = |\psi^+|^2$.

- The positron affinity is then determined as

$$A^+ = \mu^- + \mu^+\,.$$

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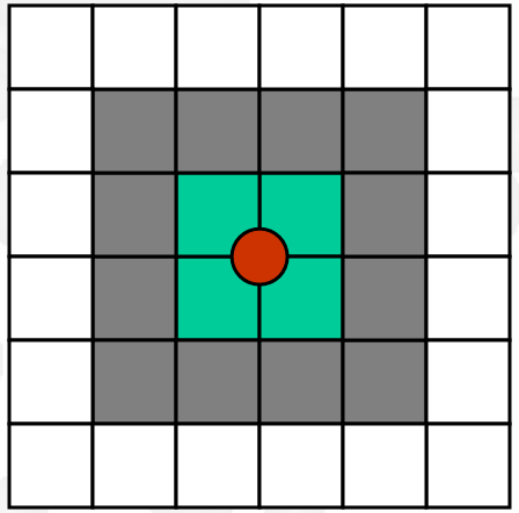
Electronic structure

- The WIEN2k code was used to obtain the electronic structure of studied systems.
- An LDA approach used for electron-electron exchange-correlations.
- This code is one of the most precise implementations of DFT for crystalline systems.
- The unit cell is divided into (non-overlapping) spheres centered at nuclei and an interstitial space.
- The 3D electron density and Coulomb potential are calculated on the regular 3D mesh covering the unit cell.
- $\nabla\rho^-$ is calculated numerically inside the unit cell (the 3D mesh for valence electrons and radial mesh for core electron densities).
- Numerical parameters (cutoff, potential and density expansions) checked carefully to warrant precise results ($\sim$0.1 ps for lifetime).

Positron calculations

- We use one of the variants of atomic superposition code to solve the Schrödinger equation for positrons using a real space method (conjugate gradient).
- The 3D density and potential produced by the WIEN2k code are read into the positron code.
- The mesh spacing of the 3D mesh should be typically $0.10 - 0.15$ a.u. in order to get precise results.
  - For defect calculations, we add additional bulk cells at the sides of the defect supercell to avoid problems with boundary conditions.
  - The electron density and potential are joined continuously at the faces of supercell.



Outline

Experimental considerations

- In positron lifetime studies there is quite larger scatter among bulk lifetime results obtained by different groups.
- We used mostly experimental results from the review by Campillo Robles and Plazaola [Defect Diff. Forum **213-215**, 141 (2003)] and added also some newer measurements.
- Differences at the level $\sim$10 ps are not rare (e.g. Al: 160–170 ps).
- For example, McGuire and Keeble [J. Appl. Phys. **100**, 103504 (2006)] have shown that using three different wrap foil materials for the source results in differences up to 6 ps in bulk lifetimes of Al, Ni, Zr, and Pb.
- This complicates comparison with calculations and raises questions about the precision of lifetime measurements.
- For defect studies, the situation is similar.

Abbreviations

- BN - Boroński and Nieminen [PRB **34**, 3820 (1986)]
- AP - Arponen and Pajanne [Ann. Phys. (N.Y.) **121**, 343 (1979)]
- GC - original GGA with AP and $\alpha = 0.22$
- SL - Stachowiak and Lach [PRB **48**, 9828 (1993)]
- SG - SL with $\alpha = 0.10$ (after Boroński [Nukleonika **55**, 9 (2010)])
- DB - Drummond et al. [PRL **107**, 207402 (2011)]
- DG - DB with $\alpha = 0.05$

- We often use notation 'X+' for the specification of experimental lifetimes' range though it is not ideal.

d-metal lifetimes (in ps)

Element	BN	AP	GC	SL	SG	DB	DG	Exp.
Fe	101	94	110	98	107	102	107	105+
Cu	106	98	120	103	114	107	113	110+
Zn	137	124	150	131	144	136	144	145+
Nb	121	111	123	116	123	121	124	120+
Ag	123	113	140	118	132	123	131	130+
W	100	92	103	97	102	101	103	105
Pt	96	89	105	93	101	97	101	99+

DG and SG give best agreement with experiment.
GC is somewhat exaggerated.
LDA approaches yield often too short lifetimes.

d-metal affinities (in eV)

Element	BN	GC	SG	DB	DG	Exp.
Fe	-4.31	-3.74	-4.03	-4.12	-3.98	-3.3
Cu	-4.89	-4.20	-4.55	-4.68	-4.50	-4.3
Zn	-5.34	-4.78	-5.07	-5.06	-4.91	
Nb	-3.99	-3.62	-3.81	-3.75	-3.65	-3.8
Ag	-5.70	-4.96	-5.34	-5.45	-5.26	
W	-2.08	-1.70	-1.90	-1.90	-1.80	-1.9
Pt	-3.95	-3.34	-3.66	-3.78	-3.62	-3.8

For affinities the situation is not that clear compared to lifetimes.

There are not so many measurements.

Resulting affinity values are influenced by the electron-electron exchange-correlation approach considered.

Alkali metal lifetimes (in ps)

Element	BN	AP	GC	SL	SG	DB	DG	Exp.
Li	300	259	283	277	295	304	316	291
Na	328	291	339	310	342	343	364	338
K	374	338	396	360	395	401	423	397

SG and GC give best agreement with experiment.
DG lifetimes fall too long.
There are doubts about the precision of original experiment
[Weisberg and Berko, Phys. Rev. **154**, 249 (1967)].

sp-metal lifetimes (in ps)

Element	BN	AP	GC	SL	SG	DB	DG	Exp.
Al	165	146	155	155	160	161	165	160+
Sn(β)	189	167	198	177	192	186	194	196+
Pb	189	167	202	177	194	187	196	200+

SG and DG give best agreement with experiment.
BN, AP, and SL lifetimes usually too short.
Less frequent measurements, data might not be always reliable.

Group IV semiconductor lifetimes (in ps)

Element	BN	AP	GC	SL	SG	DB	DG	Exp.
C	93	87	102	91	98	95	99	98+
Si	211	186	222	197	214	208	217	216+
Ge	214	190	241	201	225	213	225	219+
Sn(α)	257	228	296	242	274	258	275	289

SG and DG give best agreement with experiment.
BN, AP, and SL lifetimes usually too short.
β-Sn sample could still contain some defects.

Oxide lifetimes (in ps)

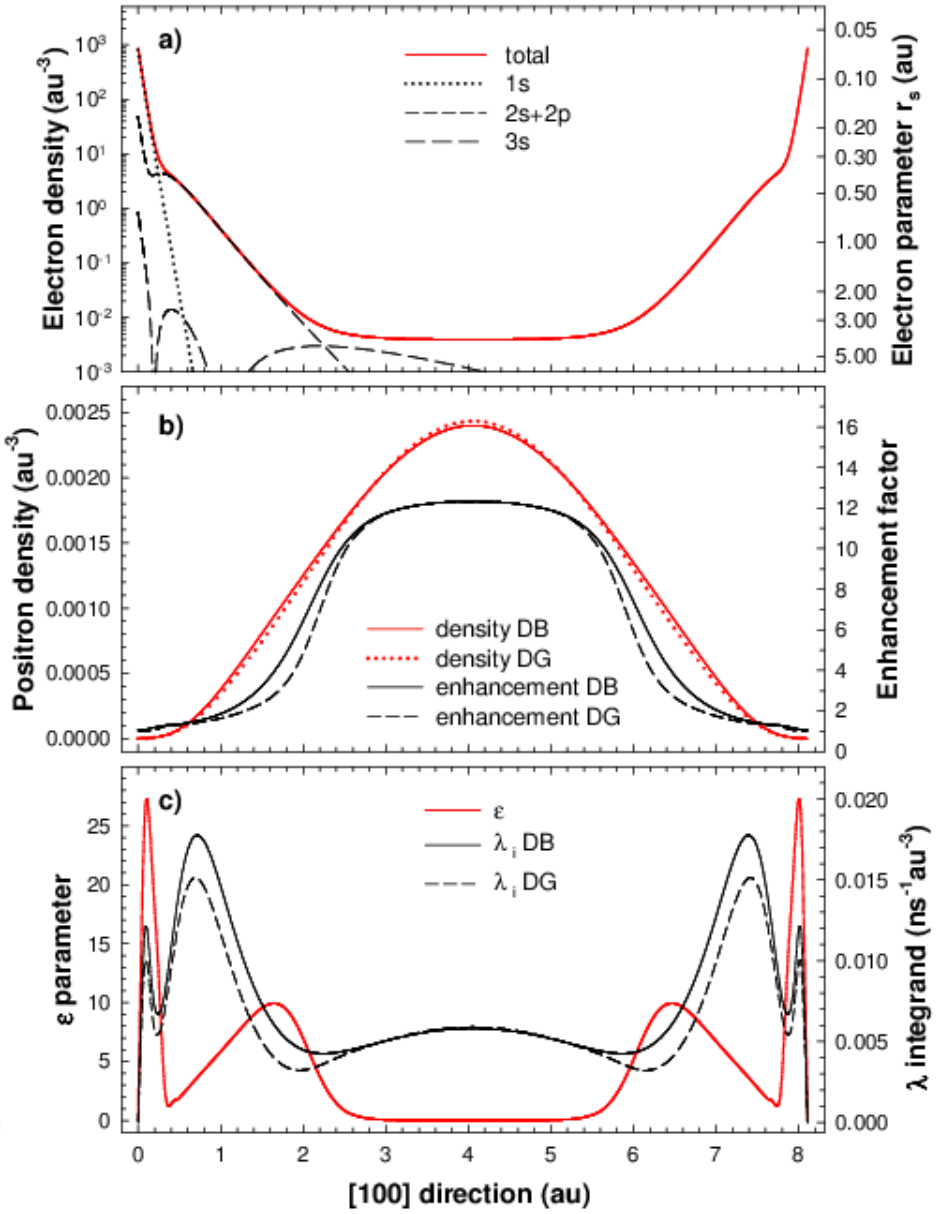
Oxide	BN	AP	GC	SL	SG	DB	DG	Exp.
MgO	118	109	145	114	132	119	128	130
Cu_2O	147	134	177	141	162	147	158	156+
ZnO	144	132	183	138	162	145	157	151+
ZrO_2	128	118	159	124	143	129	138	∼140

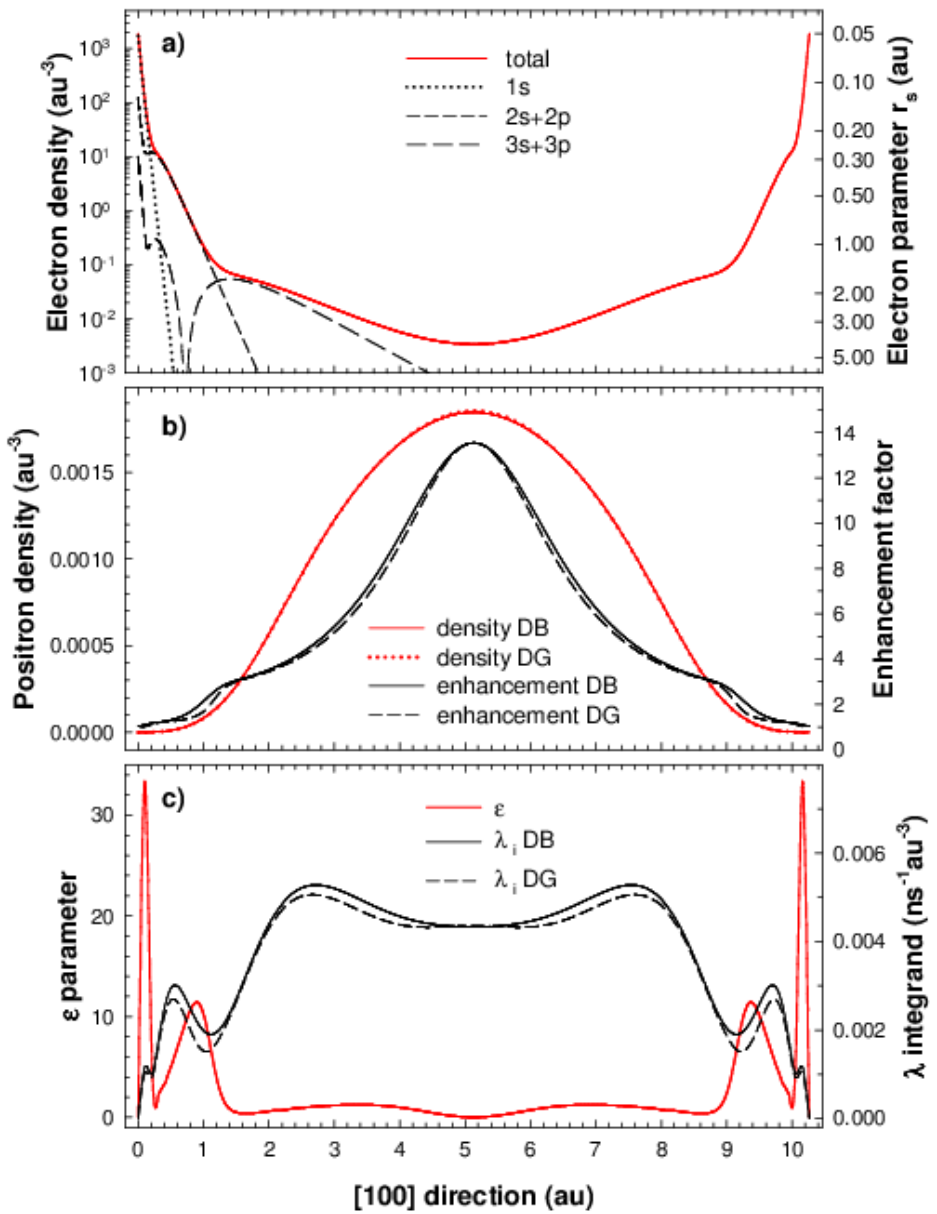
SG and DG give best agreement with experiment.
BN, AP, and SL lifetimes usually too short.
Some experimental lifetimes uncertain.

Positron GGA from the microscopic viewpoint

- A comparison of Na (bcc) and Si (diamond) electron- and positron-related quantities.
- The comparison is done for a [100] line having two atoms at its ends.
- DB and DG approaches are considered.
- Gradient correction is important in the core region and for open structures also at the interstitial space!!

Positron GGA from the microscopic viewpoint





Defect calculations

We have also examined non-relaxed single vacancies in Al, Si and Cu and calculated lifetimes for them.

Element	BN	AP	GC	SL	SG	DB	DG	Exp.
Al	234	204	222	217	227	228	233	237–244
Si	242	211	254	225	245	239	249	270–273
Cu	163	147	184	155	174	159	169	180

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Conclusions and outlook

- We have calculated positron characteristics in selected, representative solids based on reliable DFT electronic structure calculations.
- Highly accurate electronic structures of studied materials were considered.
- Several LDA and GGA approaches were tested.
- The SG and DG calculations seem to agree best with experimental lifetimes, except for alkali metals that would require new experimental data allowing for a more precise comparison.
- Positron energetics (affinities) is also improved in new GGA schemes though further studies are needed.
- The original GGA scheme appears to overestimate the gradient correction.
- Defect studies were also performed showing promising results, but relaxations still need to be considered.

Thank you!

T h a n k y o u !

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