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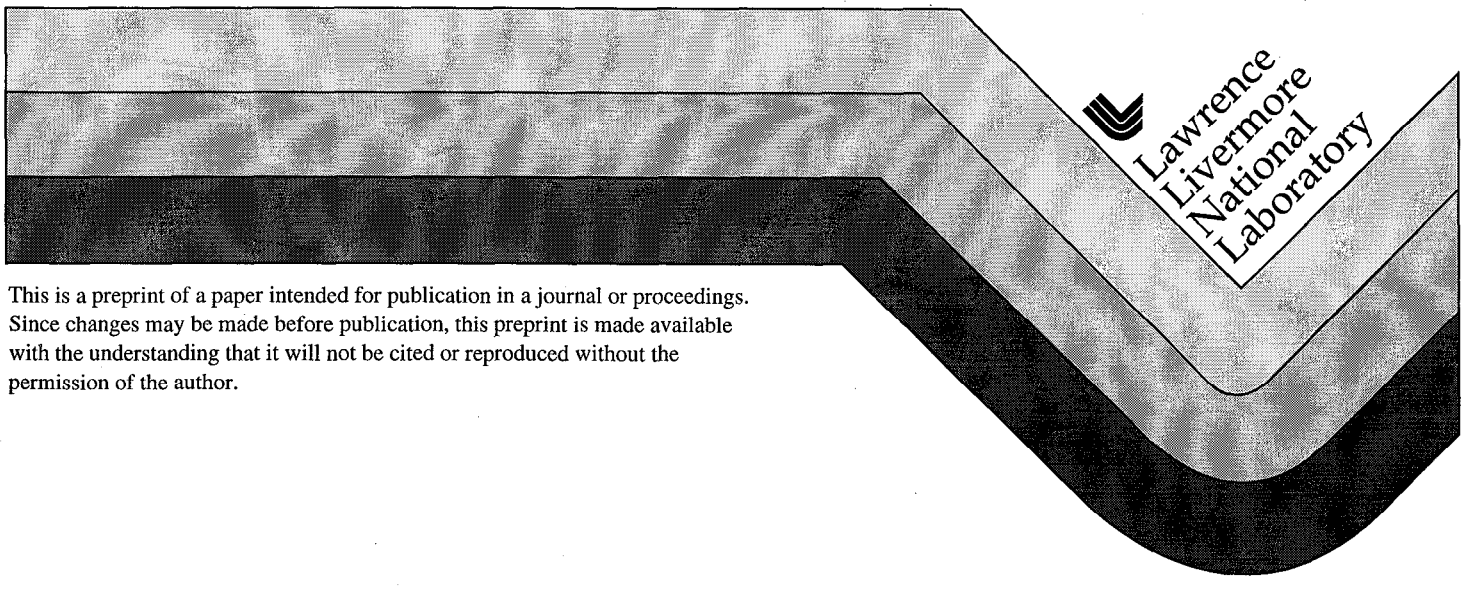

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Calculation of Positron Observables Using a Finite-Element-Based Approach

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Abstract

We report the development of a new method for calculating positron observables using a finite-element approach for the solution of the Schrodinger equation. This method combines the advantages of both basis-set and real-space-grid approaches. The strict locality in real space of the finite element basis functions results in a method that is well suited for calculating large systems of a thousand or more atoms, as required for calculations of extended defects such as dislocations. In addition, the method is variational in nature and its convergence can be controlled systematically. The calculation of positron observables is straightforward due to the real-space nature of this method. We illustrate the power of this method with positron lifetime calculations on defects and defect-free materials, using overlapping atomic charge densities.

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Keywords: Finite Element Method, Positron Lifetimes, Local Density Approximation, Monovacancies, C_{60}, Fullerenes

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Introduction

Quantum mechanical calculations of positron states in materials provide the basis for the interpretation of positron annihilation experiments such as positron lifetimes, core-electron momentum measurements, and 2D-ACAR spectra [1]. Several methods that were originally developed for electronic structure calculations have been adapted to calculate the positron distributions and related observables in periodic systems. This has been very successful for simple metallic systems, where quantitative lifetime calculations yield results that agree with experiment to within a few picoseconds [2-4]. Nevertheless, there are significant limitations in many of these approaches. Calculations based on the linear-muffin-tin orbital (LMTO) method [5,6] are well suited for electrons, but are less suitable for describing positron distributions in the interstitial region, especially for open structures that are difficult to treat in the atomic sphere approximation (ASA). In addition, traditional approaches for the solution of the Schrodinger equation result in computation times that grow with the third power of the system size, and at least quadratically in memory requirements. With currently available computers, practical calculations are limited to systems on the order of 100-200 atoms, which is often too small to model grain boundaries, dislocations, defects on surfaces, and other systems of current interest to the positron annihilation community. Although methods with better scaling have been developed [7], there is still a clear need for a new approach that is suitable for very large systems and open structures with arbitrary geometry.

This need has prompted us to develop a new method for calculating positron observables based on a finite-element (FE) approach which combines the favorable properties of both basis-set and real-space-grid approaches. This method is capable of treating very large systems of thousands of atoms with arbitrary accuracy. The method is a full-potential approach that makes no approximations to the shape of the positron potential, in contrast to ASA-based approaches like the LMTO. In this paper, we present a brief description of this method together with results of calculations on positron distributions and lifetimes in elemental metals, vacancies, and ordered pure and potassium-doped fullerenes. Our results demonstrate that this new method is very well suited for positron calculations and already provides reliable results for very large systems.

Method

The finite element method has a long history of success in diverse applications ranging from civil engineering to quantum mechanics [8,9]. There have been a number of applications to the electronic structure of atoms and molecules [10,11], but only a few to periodic solids [12-14]. We have developed a full 3-D finite-element-based approach to the solution of the Schrodinger equation with boundary conditions appropriate to a periodic solid. This approach

is developed in detail in reference [14]. Here, we summarize the approach and discuss its adaptation to positron calculations.

In the FE method, solutions to differential equations (e.g. electron or positron wavefunctions) are described in terms of strictly local, piecewise polynomial basis functions. The unit cell is partitioned into subdomains called *elements*. Local polynomials are defined in each element and these polynomials are linked continuously to neighboring elements and across the domain boundaries to create piecewise continuous functions. These piecewise continuous polynomials form the basis functions of our approach. Expansions in terms of these basis functions can be used to describe an arbitrary function throughout the unit cell, and the accuracy of this representation can be improved systematically by increasing the order of the polynomials or the number of elements. The method therefore has all the advantages and flexibility of a variational basis-set method. In addition, the piecewise continuous basis functions are strictly local in real-space, which results in sparse Hamiltonian and overlap matrices and enables the efficient use of iterative diagonalization techniques and parallel computer architectures. The method therefore combines both the computational advantages of real-space-grid methods and the variational nature and convenient expansion properties of basis-set approaches.

The number of elements required for an accurate calculation depends on the rapidity of wavefunction variation across the unit cell. Positrons typically occupy the interstitial region of the solid, with relatively modest variations in wavefunction across the unit cell, so we might expect that positron calculations can be performed fairly accurately with a small number of elements. Electron calculations with an empirical Si pseudopotential yield a band structure in excellent agreement with highly-converged plane-wave calculations with only 6x6x6 elements in the unit cell [14]. It is reasonable to expect similar, or even slightly better convergence for the positron calculations, and this is confirmed by our results reported below.

The FE method needs a positron potential in order to calculate the positron wavefunction. This potential is currently obtained in our approach from overlapping atomic calculations. The electrostatic interactions with the electrons and the nuclei provide the dominant part of the potential, and this is obtained by overlapping atomic electrostatic potentials. The remaining electron-positron correlation potential is taken from a local-density-approximation (LDA) form [2] where the potential depends only on the electron charge density, which is also obtained by overlapping atomic charge densities. We have used both an LDA form [2] based on free-electron calculations by Arponen and Pajanne [16] and a more recent modification using a Generalized Gradient Approximation (GGA) [4]. The overlapping atomic charge density approach [17] has been used successfully to treat fairly large systems (of order 256 atoms) in finite-difference calculations of positrons in solids [18]. At present, our positron

calculations do not allow for electron or positron charge self-consistency, although this is planned for the future. This lack of self-consistency and uncertainties in the electron-positron interactions are the most significant limitations of the current implementation.

Given a positron potential, the FE method can solve the Schrodinger equation for the lowest-energy positron state, and the positron charge density is obtained directly in real-space from the wavefunction expansion. The positron lifetime depends on the product of the electron and positron charge densities integrated over the unit cell together with an enhancement function that depends on the total electron density [1-4]. The enhancement function is again obtained from an LDA [1-3] or GGA [4] form.

Matrix elements and other integrals over the unit cell such as positron lifetimes are easy to calculate in the FE approach, since the basis functions have a simple polynomial form, and resulting wavefunctions and related quantities are uniquely defined at all points in the unit cell in terms of the polynomial coefficients in the wavefunction expansion. This simple expansion property and the direct real-space nature of the method makes the calculation of positron observables straightforward. The current implementation provides positron distributions and lifetimes, and we plan to add calculation of electron-positron momentum densities in the near future.

Positron lifetimes in metals and monovacancies

Calculations of positron lifetimes in elemental metals provide a useful test of the reliability of any new method for positron calculations. Figure 1 shows a comparison between positron lifetimes calculated in the FE-LDA approach and those obtained using a traditional LMTO-ASA approach, both with the same local density form for the potential [2]. The corresponding FE, LMTO, and experimental lifetimes are given in Table 1, together with FE results using the GGA potential. The FE-LDA approach yields lifetimes that are in very good overall agreement with the LMTO method, although they tend to be slightly longer by about 1-5 ps. This may be due to differences in the calculational details: the FE calculations are non-self-consistent while the LMTO calculations are based on self-consistent charge densities, and the FE calculations make no approximations to the shape of the potential while the LMTO calculations use the ASA. The calculations were performed for 4x4x4-, 6x6x6-, and 8x8x8-element meshes. In all cases the calculated lifetimes were essentially converged for the 4x4x4 calculation, with changes in lifetimes of less than 0.5% and typically on the order of 0.1% with increasing numbers of elements. The most highly converged calculations (8x8x8) are reported in Table 1.

The GGA results in Table 1 are in reasonable agreement with the calculations of Ref. [4] which used the same GGA functional within a finite difference method based on atomic

superposition. There is excellent agreement for many of the elements, but there are significant differences for some transition metals which may be due to the choice of electronic configuration in the atomic calculations. Ref. [4] used atomic ground state configurations while the present calculation used configurations that more closely reflect the electronic structure of the solid. The overall agreement is still very good and confirms the accuracy the method for positron lifetime calculations.

Table 1 also lists results for monovacancy lifetimes in Al, Cu, and Ag based on 31-atom supercells. The agreement with experiment is very good, although the FE method slightly underestimates the experimental lifetime values. The calculated values increase slightly to give better agreement with experiment when larger supercell sizes are used for the monovacancy calculations.

It is known that calculated monovacancy lifetimes are sensitive to the supercell size [18], and the 31-atom calculations listed in table 2 are not quite converged with respect to supercell size. We have examined the convergence of the Al monovacancy with respect to both supercell size and the number of elements per unit cell. The results are shown in table 2. Note that the system is well converged to a value of 243 ps, very close to the experimental value of 244 ps, with 16 elements per primitive unit cell and a 255 atom supercell. This convergence is confirmed by the absence of any further change in the lifetime upon increasing either the number of elements or the supercell size, or both. The largest supercell calculations for an 863-atom unit cell were well within the range of out FE implementation, indicating that the method is well suited for problems that require large system sizes, such as dislocations and other extended defects.

Positrons in potassium-doped fullerenes

The FE method has three significant advantages over our previous LMTO-ASA method. First, it is capable of treating very large systems, as illustrated by the 863-atom unit cell calculations for an Al monovacancy. Second, it is well suited for treating open structures where the atomic sphere approximation may give a poor description of the electron and positron charge distributions. Third, it provides a full three-dimensional representation of the positron distribution in real space, in contrast the the LMTO which distorts the representation of space through the atomic sphere approximation. All three of these advantages are illustrated here by a set of positron calculations on the low temperature structure of solid C_{60} with and without potassium doping.

Solid C_{60} fullerene forms a face-centered cubic structure at higher temperatures with the carbon fullerene molecules randomly oriented with respect to each other. At lower temperatures, the molecules orient to form a simple cubic structure consisting of four C_{60}

molecules to give a 240 atom unit cell. Potassium doping first fills the octahedral sites between the fullerene molecules (KC_{60}) and with increasing doping, the tetrahedral sites are also occupied by potassium atoms (K_3C_{60}), resulting in a compound that exhibits high temperature superconductivity[19]. Puska and Nieminen [20] have performed positron calculations on this system using a finite difference method [17]. They used a simplified structure for the C_{60} orientation so that they could treat the system as face-centered cubic with a single fullerene molecule. We compare their results with our calculations based on the larger 240-atom simple cubic structure.

Puska and Nieminen obtained lifetime values of 327, 276, and 261 picoseconds for C_{60}, KC_{60}, and K_3C_{60}, respectively. Using a similar LDA enhancement and correlation function, we calculate corresponding lifetime values of 330, 273, and 261 picoseconds, in excellent agreement with the earlier results.

Calculations of the positron distribution indicate that the positron does not enter the fullerene molecule, but prefers to sit mostly in the octahedral site and partly in the tetrahedral site between molecules [20] . Potassium also preferentially occupies these octahedral sites, so the repulsion between the potassium nucleus and the positron will force a redistribution of the positron charge density in the material with doping. This is illustrated in Figure 2. With no potassium, the positron charge is localized in the octahedral site, and avoids the open space at the center of the fullerene molecule. Once the octahedral site is occupied by a potassium atom (KC_{60}), the positron concentrates in the tetrahedral sites, still avoiding the centers of the fullerene molecules. When potassium atoms occupy the tetrahedral sites as well, the positron squeezes between the tetrahedral and octahedral site, and also shows a small buildup inside the fullerene molecule. The calculated positron lifetime changes with the potassium doping due to the redistribution of the positron charge density and the resulting change in the electron-positron charge density overlap.

Conclusions

We have successfully applied a new finite element electronic structure technique to calculate positron distributions and lifetimes in a variety of systems including elemental metals, vacancies in metals, and fullerene structures. Our FE approach has demonstrated its efficiency and applicability to very large systems by calculating the positron lifetime in an 863-atom monovacancy structure, and larger calculations are feasible. The method is also well suited to calculations on open structures, as demonstrated by the results on potassium-doped fullerenes. The method readily provides positron distributions in real space that facilitate an understanding of the positron sensitivity to specific parts of the unit cell, and the polynomial basis functions make it easy to calculate positron observables such as lifetimes and momentum

densities in real space. This approach is already a valuable method for performing positron calculations on very large systems, and promises to become even more powerful once charge self-consistency is implemented.

Acknowledgments

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Figure Captions

1. Comparison of positron lifetimes (in picoseconds) calculated in the LMTO-ASA and FE methods, using the same LDA form for the electron-postron correlation and enhancement. See Table 1 for more details.

2. Positron charge distributions along the simple cubic (111) direction for potassium doped fullerenes: (a) C_{60}, (b) KC_{60}, (c) K_3C_{60}. Octahedral and tetrahedral sites are indicated and the end points are located at the centers of fullerene molecules.

Tables

Table 1.

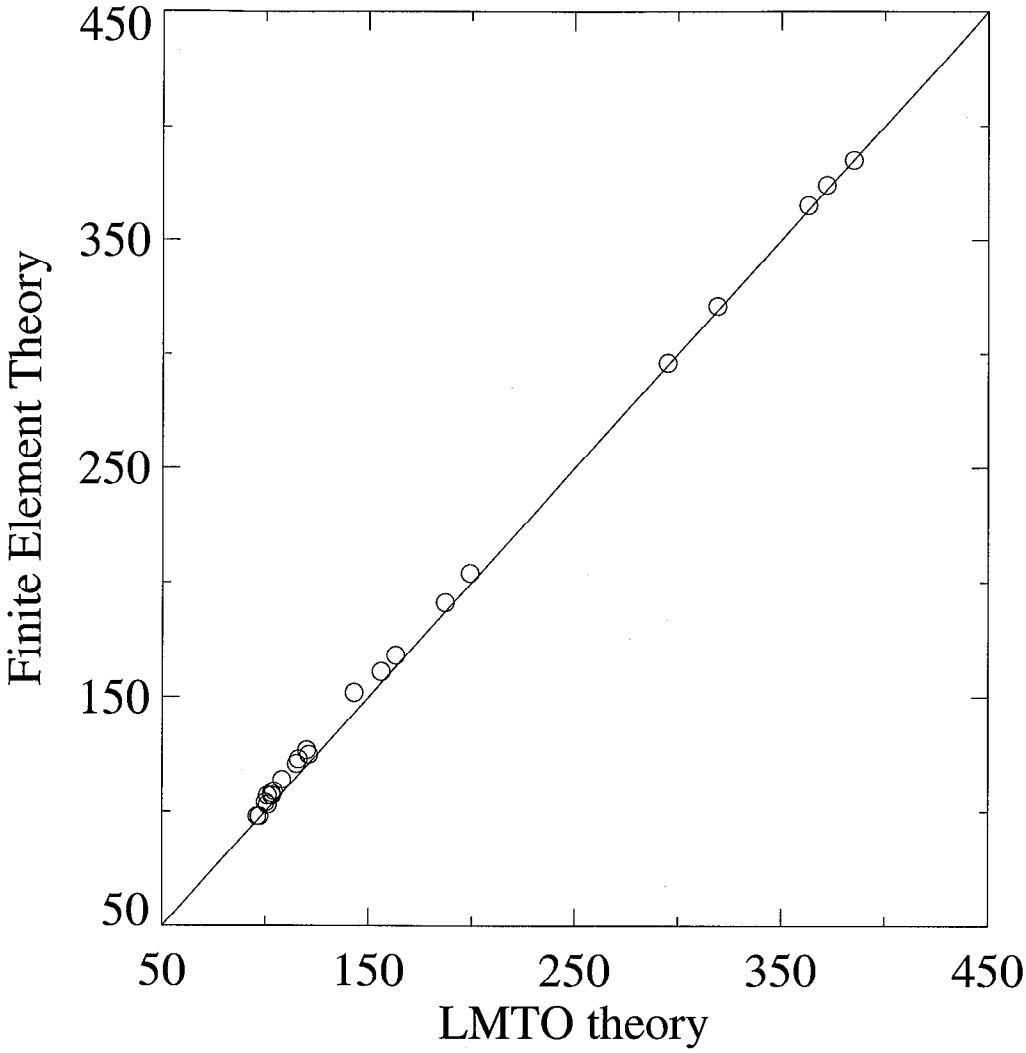
Positron lifetimes in picoseconds for selected elemental metals and monovacancies. LMTO calculations are taken from reference [2] using the same LDA electron-positron correlation potential and enhancement function as the present FE-LDA calculations. The GGA calculations use the functional form described in Ref [4] with alpha=0.22. Monovacancy calculations were performed with unrelaxed atomic positions.

Element	LMTO	FE-LDA	FE-GGA	Expt.
Li	295	296	283	291
Na	319	321	341	338
K	363	365	400	397
Rb	372	374	418	406
Cs	385	385	434	418
Al	163	168	159	163
Pb	187	191	213	194
Ti	143	152	164	147
V	115	121	132	130
Cr	101	103	110	120
Fe	101	107	120	106
Ni	97	98	108	110
Cu	103	107	119	110
Zr	156	161	162	165
Nb	121	125	128	119
Mo	104	109	112	103
Pd	103	108	122	96
Ag	120	127	149	131
Ta	116	123	130	116
W	100	104	108	105
Pt	96	98	106	99
Au	108	114	131	117
Gd	199	204	213	230
Vacancies				
Cu	164	169	---	173
Al	234	239	---	244
Ag	194	199	---	198

Table 2.

Convergence results for a monovacancy in Al. The calculated lifetimes are in picoseconds. The horizontal axis gives the number of elements per primitive unit cell. For the 255 atom case, 16 elements/unit cell corresponds to a 16x16x16 calculation in the supercell.

number of atoms	Elements/unit cell		
	2	16	54
31	242	240	239
255	245	243	243
863	245	243	243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350
250
150
50
Finite Element Theory
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LMTO theory

Fig 1
Sterne

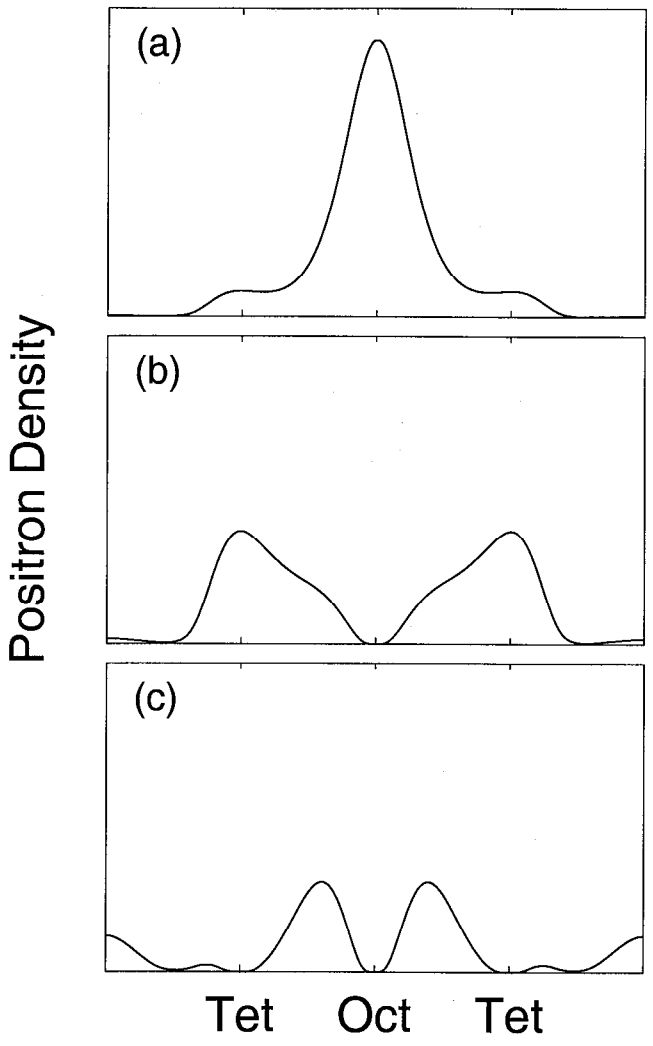

Fig 2

Sterne