Visualization of atomic-scale phenomena in superconductors: application to FeSe

Peayush Choubey¹, T. Berlijn¹,², A. Kreisel¹, C. Cao³ and P. J. Hirschfeld³

¹Department of Physics, University of Florida, Gainesville, Florida 32611, USA
²Center for Nanophase Materials Sciences and Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
³Condensed Matter Physics Group, Department of Physics, Hangzhou Normal University, Hangzhou 310036, China

(Dated: February 3, 2014)

We propose a simple method of calculating inhomogeneous, atomic-scale phenomena in superconductors which makes use of the wave function information traditionally discarded in the construction of tight-binding models used in the Bogoliubov-de Gennes equations. The method uses symmetry-based first principles Wannier functions to visualize the effects of superconducting pairing on the distribution of electronic states over atoms within a crystal unit cell. Local symmetries lower than the global lattice symmetry can thus be exhibited as well, rendering theoretical comparisons with scanning tunneling spectroscopy data much more useful. As a simple example, we discuss the geometric dimer states observed near defects in superconducting FeSe.

PACS numbers: 74.20.-z, 74.70.Xa, 74.62.En, 74.81.-g

In the past two decades, two developments have spurred new interest in atomic-scale effects in superconductors. The first is the discovery of systems, like the high-$T_c$ cuprates, heavy fermion, and Fe-based superconductors, with very short coherence lengths $\xi$, which in the cuprates approach the unit cell size. The second is the ability to image atomic- and even sub-atomic scale features in scanning tunneling spectroscopy (STS). Comparison of such images with theory has sometimes been frustrating, since STS images often contain much more detail than that predicted by current calculations.

The success of the semiclassical theory of superconductivity [1, 2], which integrates out rapid oscillations of the pair wave function at the atomic-scale, has led to the widespread notion that atomic scale effects are irrelevant for superconductivity. However, observation of the electronic structure very near a defect or surface reflects directly the symmetry and structure of the superconducting order parameter, and can furthermore provide information on gap inhomogeneity, vortex structure, competing phases, and even the atomic-scale variation of the pairing interaction. Yet in the currently available method used to describe inhomogeneous phenomena, the Bogoliubov-de Gennes equations, atomic wave function information is typically integrated out by adopting a tight-binding model for the normal state electronic structure.

There is now a growing list of problems which seem to require atomic scale “details” beyond the BdG description usually employed. For example, STS images of underdoped cuprates show the existence of unusual incommensurate electronic modulations, proposed to represent real-space images of the pseudogap, which have alternating high and low intensity on O-centered bonds between neighboring Cu’s [3-5]; such effects cannot be captured by conventional models which include Cu states only. The importance of obtaining intra-unit cell information for this problem has been stressed, e.g. in Ref. [6]. As a second example, there is still no consensus on the origin of the STS pattern around a Zn impurity in cuprates, which displays a central intensity maximum on the Zn site, unlike simple models of the response of a $d$-wave superconductor to a strong potential [7]. A popular explanation relies on “filter” effects which describe a nontrivial tunneling process from the surface to the CuO plane [8, 9], but while there is some support for these ideas from first principles calculations in the normal state [10], there has been until now no way to include both superconductivity and the various atomic wave functions in the barrier layers responsible for the filter [11]. Finally, in Fe-based superconductors a variety of defect states observed by STS in FeSe, LiFeAs, NaFeAs and other materials [12-17] break the square lattice symmetry locally and therefore cannot be described by Fe-only lattice BdG calculations. These include so-called “geometrical dimer” structures aligned with the As or Se states at the surface.

In this work, we present a simple technique which restores the intra-unit cell information lost in the construction of the Bogoliubov-de Gennes Hamiltonian, including the degrees of freedom corresponding to other atoms in the unit cell, as well as neighboring cells. In weak-to-intermediate coupling systems, the method dramatically improves the ability of theory to quantitatively describe intra-unit cell problems, as we illustrate by presenting the solution to the FeSe problem described above. In strongly coupled systems like cuprates, it should still be valid for symmetry-related questions.

We first introduce the elementary expression for the local continuum Green’s function in terms of the BdG lattice Green’s function which is needed for the calculation of the local density of states (LDOS) relevant for the STS experiments. We then show that the nonlocal terms also contribute and can be important even for the local continuum LDOS. We present a tight-binding model
for FeSe derived from Density Functional Theory (DFT) and corresponding Wannier basis. Within a 10-Fe-orbital BdG calculation, we calculate the response of the superconductor to a single pointlike impurity potential on an Fe site, and compare to the continuum LDOS calculated using the Wannier states. The geometric dimer states are shown to emerge naturally from this description. Finally, we discuss the approximations that we have made, as well as how the method can be improved and extended in the future.

Method. The tight binding model, while often treated as phenomenological, is in principle derived from Wannier orbitals based on first principles calculations. In order to preserve the desired mutual orthogonality of these orbitals, they are constructed from atomic wave functions on atoms in more than one unit cell, although they are exponentially localized. In a crystal with more than one type of atom per unit cell, Wannier orbitals may represent linear combinations of wave functions from more than one atomic species. Here we first construct from the DFT wave functions a basis \(w_{R,\mu}(\mathbf{r})\) using a projected Wannier method which preserves the local symmetry of the atomic states \(\alpha\). Here \(\mu\) is an orbital index, \(\mathbf{R}\) labels the unit cell, and \(\mathbf{r}\) describes the continuum position. In Fig. 1 we show examples of the Wannier Fe-d orbitals on the Fe(I) and Fe(II) sites derived for the homogeneous FeSe system, using the Fe-d bands within the energy range \([-2.5, 3]\) eV obtained from DFT using Wien2K. It is clear that, while these functions have features easily associated with the form of the corresponding atomic orbitals, they are considerably more complex, and involve significant contributions from the Se states integrated out in the downfolding, with clear differences between Fe(I) and Fe(II). These Wannier functions are used to derive the tight-binding model containing Fe site energies and hoppings in the usual way to yield the Hamiltonian

\[
H_0 = \sum_{\mathbf{R},\mu,\sigma} t^{\mu\sigma}_{\mathbf{R},\mathbf{R}'} c_{\mathbf{R},\mu,\sigma}^\dagger c_{\mathbf{R}',\mu,\sigma} - \mu_0 \sum_{\mathbf{R},\sigma} n_{\mathbf{R},\sigma},
\]

where \(t^{\mu\sigma}_{\mathbf{R},\mathbf{R}'}\) are hopping elements between orbitals \(\mu\) and \(\nu\) in unit cells \(\mathbf{R}\) and \(\mathbf{R}'\). The full Hamiltonian for a superconductor in the presence of an impurity is therefore

\[
H = H_0 + H_{\text{BCS}} + H_{\text{imp}},
\]

with the superconducting order parameter

\[
\Delta^{\mu\nu}_{\mathbf{R}\mathbf{R}'} = \Gamma^{\mu\nu}_{\mathbf{R}\mathbf{R}'} \langle c_{\mathbf{R}'\nu}\dagger c_{\mathbf{R}\mu}\rangle ,
\]

and

\[
H_{\text{imp}} = \sum_{\mu\sigma} \delta^{\mu\sigma}_{\mathbf{R}^*} c_{\mathbf{R}'\mu,\sigma}^\dagger c_{\mathbf{R}\mu,\sigma} + H.c.,
\]

where \(\mathbf{R}^*\) is the impurity unit cell, \(\mu\) runs only over the 5\(d\) orbitals associated with the impurity Fe site, and for simplicity we have taken the impurity potential \(\delta^{\mu\sigma}_{\mathbf{R}^*}\) to be nonmagnetic and proportional to the identity in the orbital basis. Here \(\Gamma^{\mu\nu}_{\mathbf{R}\mathbf{R}'}\) is the pairing interaction in orbital and real space. The inhomogeneous mean field BdG equations for this Hamiltonian may now be solved by diagonalization with the auxiliary self-consistency equation for the gap \(\Delta^{\mu\nu}_{\mathbf{R}\mathbf{R}'}\) to obtain the BdG eigenvalues \(E_n\) and eigenvectors \(u_n\) and \(v_n\).

From these we can construct the usual retarded lattice Green’s function

\[
G^{\mu\nu}_{\alpha\beta}(\mathbf{R}, \mathbf{R}' ; \omega) = \sum_{n} \left( \frac{u_{n\alpha}^* v_{n\beta}}{\omega - E_n + i0^+} + \frac{v_{n\beta}^* u_{n\alpha}}{\omega + E_n - i0^+} \right) .
\]

Under a wide set of conditions, an STS experiment at bias \(V = \omega/e\) measures the local density of states \(\rho(\mathbf{r}, \omega) = -\frac{1}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r} ; \omega)\), related to the retarded continuum local Green’s function \(G(\mathbf{r}, \mathbf{r}' ; \omega)\). To relate the lattice and continuum Green’s functions, one constructs the Matsubara Green’s function \(G(\mathbf{r}, \mathbf{r}' ; \omega_n)\) \(\equiv -\frac{1}{\pi} \text{Im} G(\mathbf{r}, \mathbf{r}' ; \omega)\) as the sum

\[
G(\mathbf{r}, \mathbf{r}' ; \omega_n) = -\sum_{\mathbf{R}} c_{\mathbf{R}\mu}(\mathbf{r}) w_{\mathbf{R},\mu}(\mathbf{r}) c_{\mathbf{R}'\mu}(\mathbf{r}'),
\]

where \(c_{\mathbf{R}\mu}\) destroys an electron in a Wannier orbital \(\mu\) in unit cell \(\mathbf{R}\), yielding

\[
G(\mathbf{r}, \mathbf{r}' ; \omega) = \sum_{\mathbf{R},\mu,\nu} G^{\mu\nu}(\mathbf{R}, \mathbf{R}' ; \omega) w_{\mathbf{R}\mu}(\mathbf{r}) w_{\mathbf{R}'\nu}(\mathbf{r}').
\]

Note that even the local continuum Green’s function \(G(\mathbf{r}, \mathbf{r} ; \omega)\) includes nonlocal and orbitally nondiagonal lattice Green’s function terms \(G^{\mu\nu}(\mathbf{R} \neq \mathbf{R}' ; \omega)\).

**Application to FeSe.** To illustrate the utility of this new method, we consider the general question of impurity...
states in Fe-based superconductors, which often exhibit unusual spatial forms. In particular, geometric dimers, high intensity conductance or topographic features localized on the sites of the two pnictide or chalcogenide atoms neighboring an Fe site, are ubiquitous in a number of Fe-based materials. It is not known whether these defects are Fe vacancies, adatoms or site switching, but they seem to be centered on a given Fe(I) or Fe(II) site, as imaged by STM topography, and it is natural to assume that the impurity state is coupled to the pnictide or chalcogenide atoms closest to the surface, i.e. the defects are oriented one way or another according to whether they are centered on Fe(I) or Fe(II). We consider here the effect of a strong local repulsive potential on the Fe site, to crudely model a vacancy, site switching, or adatom, in the FeSe material ($T_c = 8$ K).

We now consider the form of the superconducting gap, which is not well-established for this system. The STS tunneling for thin films of FeSe on graphite is V-shaped at low energies, implying the presence of gap nodes or small minimum gap. We note, however, that Ref. [24] has proposed that nodes may arise from a weak SDW state present in these films. This scenario is indeed consistent with the \( \sim 16a_0 \) long “electronic dimers”, high intensity spots observed with axes aligned at 45 degrees with respect to the geometrical dimers, which have been interpreted as emergent defect states in an ordered magnetic phase [25]. However since we are primarily interested in exhibiting the local $C_4$ symmetry breaking effects due to ligand atoms possible within our current method, we ignore the possible effects of magnetism in this work, and calculate the real space pair potentials $\Gamma_{\mu \nu}^{RR'}$ within the fluctuation exchange approximation using the 10-orbital tight-binding band structure with $U = 0.955$ eV and $J = U/4$, following the procedure described in Ref. [26].

The 10-orbital BdG equations are then solved on 15 x 15 unit cell lattices with stable solutions found through iterations of the self-consistency equation for the real space gaps $\Delta_{\mu \nu}^{RR'} = \sum_{\alpha \beta} \Gamma_{\mu \nu}^{RR'} \sum_n \bar{n}_{\alpha \beta}^{R \bar{R}} \bar{f}(E_n)$, where $\sum_n$ denotes summation over all eigenstates $n$. When calculating the LDOS we use 20 x 20 supercells to acquire spectral resolution of order \( \sim 0.5 \) meV. The orbital character of the normal state DOS obtained within our calculation of FeSe electronic structure, along with the total superconducting state DOS for the homogeneous system is shown in Fig. 2b). The superconducting ground state is found to be of the usual multiband $s_{\pm}$ type. Its DOS reflects the several different orbital gaps in the problem, and bears a striking resemblance to the nearly V-shaped conductance observed in experiment [12]. Note, however, that the overall gap magnitude is much larger than in experiment, since we have chosen artificially large interaction parameters to deliberately create a unrealistically large gap, so that impurity bound states may be more clearly visualized within our numerical resolution. Since the normal state density of states for this material is flat at low energies, we do not expect this to alter our results qualitatively, although the exact value of the impurity potential which creates a bound state for a realistic gap size will change.

**Single impurity in FeSe.** We now add a single impurity to the system, of strength $V_{\text{imp}} = 5$ eV in all orbital channels $\mu$, which creates an impurity bound state within the spectral gap at $\pm \Omega_0 \sim 8.4$ meV (Fig. 2b), although the spatial distribution of spectral weights of the posi-
tive and negative states are quite different. Such bound states are not universal, but depend on the electronic structure of the host, impurity potential details, and gap functions, as has been emphasized in Refs. [18] and [24]. The structure of this complex bound state extends above and below the Fe plane, as can now be visualized by the current method.

In Fig. 2(c,d), we show first the local lattice density of states $\rho_{\text{BdG}}(\mathbf{r}, \omega) \equiv -\frac{1}{\pi} \text{Im} \ G(\mathbf{r}, \mathbf{R}; \omega)$ obtained at the positive and negative resonance energies within a conventional 10-Fe orbital BdG calculation. As is clear, both resonance patterns are $C_4$ symmetric as they must be for the tetragonal FeSe system, and do not resemble any defect states imaged in STS experiments on this system. On the other hand, in Fig. 3 we plot the analogous continuum LDOS $\rho(\mathbf{r}, \omega) \equiv -\frac{1}{\pi} \text{Im} \ G(\mathbf{r}, \mathbf{r}; \omega)$, which extends in three dimensions, although the set of $\mathbf{R}$ considered here lies in a 2D plane, due to the 3D spatial extent of the Wannier functions. Cuts at various $z$ from $z = 0$ in the Fe plane to a point very close to the Se plane are shown. As expected, in the Fe plane $\rho(\mathbf{r}, \omega)$ is still $C_4$ symmetric (Fig. 2a,b), but when one increases $z$ the local placement of the Se atoms breaks this symmetry to $C_2$, as clearly seen in the figure for $z$ close to the Se positions. Indeed, it is natural to suppose that STS measurements will correspond roughly to a choice of $z$ close to the value of the exposed Se layer. A comparison of the resonance patterns Fig. 3(c,d) with the corresponding Fe-only BdG LDOS patterns in Fig. 2(c,d) suggests a simple explanation of the patterns, namely that intensity maxima occur on those Se sites associated with the resonant Fe Wannier orbitals, with intensities on these Se sites adding constructively, as in the cartoons in Fig. 3 (c,d). Although this crude guess works reasonably well for the positive energy dimer Fig. 3(d), some discrepancies are seen in the negative energy image Fig. 3(c). Indeed, deviations are in general to be expected, since simply adding intensities from resonant sites neglects contributions from nonresonant ones, as well as from nonlocal terms $\mathbf{R} \neq \mathbf{R}'$, $\nu \neq \mu$ in the continuum Green’s function arising in Eq. (5). The importance of these terms is illustrated in Fig. 3(c), where the local, orbitally diagonal contributions are plotted alone for a cut just above the Fe plane. The true, significant symmetry breaking is only recovered in the full result Fig. 3(f).

**Discussion.** The orientation of the “geometric dimer” seen at resonance in Fig. 3(d) agrees with experiment [12] in that it is oriented along the Fe-As bond, and will alternate orientation for defects located on Fe(I) and Fe(II) sites. Other comparisons with experiment are difficult, as detailed spectral features of these states are not yet available. We note, however, that while the results presented here correspond to a low-energy resonant state created by the opening of the superconducting gap, nonresonant impurity states with similar patterns should be visible at higher energy and be considerably broader due to their coupling to the metallic continuum. In fact, it is clear from Fig. 2(d) that dimer-like patterns should be visible at positive bias up to energies significantly larger than maximum gap. Such states can be studied more accurately within the current technique by self-consistently downfolding $H_0 + H_{\text{imp}}$ onto an inhomogeneous tight-binding model and thereby generating an inhomogeneous set of Wannier functions $w_{\mathbf{R},\mu}(\mathbf{r})$. Since in some systems the geometric dimer states are visible in topography, they may also correspond to local increases in height of As/Se relative to the homogeneous surface; these effects can be captured by allowing the lattice to relax around the impurity atom before downfolding onto a tight-binding model. Extensions of the current method along these lines are in progress.

**Conclusions.** We have introduced a method to enable theoretical visualization of inhomogeneous states in superconductors, combining traditional solutions of the Bogoliubov-de Gennes equations with a first principles Wannier analysis. The method not only enables a
much higher spatial resolution, but also captures the local symmetry internal to the unit cell of the crystal. Furthermore the method incorporates the nonlocal lattice Green’s function contributions, which we have demonstrated to be of qualitative importance. As an example, we showed how “geometric dimer” impurity states seen in Fe-based superconductors can be understood as consequence of simple defects located on the Fe site due to the hybridization with the pnictogen/chalcogen states. In terms of both symmetry and higher spatial resolution, the result obtained with the method introduced here represents a qualitative improvement over conventional BdG investigations, and opens a new window on the theoretical analysis of atomic scale phenomena in superconductors.

Acknowledgements. The authors are grateful to B.M. Andersen, H.P.-Cheng, M.N. Gastiasoro, J. Hoffman, W. Ku, C.-L. Song, and Y. Wang for useful discussions. PC, AK, and PJH were supported by DOE DE-FG02-05ER46236, CC by NSFC 11274006, and TB by DOE CMCSN DE-AC02-98CH10886 and as a Wigner Fellow at the Oak Ridge National Laboratory. The authors are grateful to W. Ku for use of his Wannier function code.

[1] G. Eilenberger, Z. Phys. 214, 195 (1968).
[2] J. Serene and D. Rainer, Phys. Rep. 104, 221 (1983).
[3] C. Howald, H. Eisaki, N. Kaneko, M. Greven, and A. Kapitulnik, Phys. Rev B 67, 014533 (2003).
[4] T. Hanaguri, C. Lupien, Y. Kohsaka, D. -H. Lee, M. Azuma, M. Takano, H. Takagi and J. C. Davis Nature 430 (2004).
[5] Y. Kohsaka, C. Taylor, K. Fujita, A. Schmidt, C. Lupien, T. Hanaguri, M. Azuma, M. Takano, H. Eisaki, H. Takagi, S. Uchida, and J. C. Davis, Science 315, 1380 (2007).
[6] M. J. Lawler, K. Fujita, Jiinhwann Lee, A. R. Schmidt, Y. Kohsaka, Chung Koo Kim, H. Eisaki, S. Uchida, J. C. Davis, J. P. Sethna and E.-A. Kim, Nature 466, 347 (2010).
[7] For reviews see A. V. Balatsky, I. Vekhter, and J.-X. Zhu, Rev. Mod. Phys. 78, 373 (2006); H. Alloul, J. Bobroff, M. Gabay and P.J. Hirschfeld, Rev. Mod. Phys. 81, 45 (2009).
[8] J.-X. Zhu, C. S. Ting, and C. R. Hu, Phys. Rev. B 62, 6027 (2000).
[9] I. Martin, A. V. Balatsky, and J. Zaanen, Phys. Rev. Lett. 88, 097003 (2002).
[10] L.-L. Wang, P. J. Hirschfeld, and H.-P. Cheng, Phys. Rev. B 72, 224516 (2005).
[11] Note J. Nieminen et al., Phys. Rev. B 80, 134509 (2009) discussed the tunneling in cuprates with a formalism similar in spirit to the one used here, but did not apply it to inhomogeneous problems.
[12] C.-L. Song, Y.-L. Wang, P. Cheng, Y.-P. Jiang, W. Li, T. Zhang, Z. Li, K. He, L. Wang, J.-F. Jia, H.-H. Hung, C. Wu, X. Ma, X. Chen, and Q.-K. Xue, Science 332, 1410 (2011).
[13] S. Grothe, S. Chi, P. Dosanjh, R. Liang, W. N. Hardy, S. A. Burke, D. A. Bonn, and Y. Pennecl, Phys. Rev. B 86, 174503 (2012).
[14] T. Hanaguri, private communication.
[15] X. Zhou, C. Ye, P. Cai, X. Wang, X. Chen, and Y. Wang, Phys. Rev. Lett. 106, 087001 (2011).
[16] C.-L. Song, Y.-L. Wang, Y.-P. Jiang, L. Wang, K. He, X. Chen, J. E. Hoffman, X.-C. Ma, and Q.-K. Xue, Phys. Rev. Lett. 109, 137004 (2012).
[17] E.P. Rosenthal, E.F. Andrade, C.J. Arguello, R.M. Fernandes, L.Y. Xing, X.C. Wang, C.Q. Jin, A.J. Millis, and A.N. Pasupathy, arXiv:1307.3526.
[18] R. Beaird, I. Vekhter, J.-X. Zhu, Phys. Rev. B 86, 140507 (2012).
[19] A. Kokalj, Comp. Mater. Sci. 28 155 (2003).
[20] W. Ku et al., Phys. Rev. Lett. 89, 167204 (2002).
[21] P. Blaha et al., Comput. Phys. Commun. 147, 71 (2002).
[22] J. Tersoff and D.H. Hamman, Phys. Rev. B 31, 805 (1985).
[23] V. I. Anisimov et al., Phys. Rev. B 71, 125119 (2005).
[24] S.Y.Tan, M.Xia, Y.Zhang, Z.R.Ye, F.Chen, X.Xie, R.Peng, D.F.Xu, Q.Fan, H.C.Xu, J.Juan, T.Zhang, X.C.Lai, T.Xiang, J.P.Hu, B.P.Xie, D.L.Feng, Nat. Mat. 12, 634 (2013).
[25] M. N. Gastiasoro, P. J. Hirschfeld, and B. M. Andersen, arXiv:1307.4913.
[26] M.N. Gastiasoro, P.J. Hirschfeld, and B.M. Andersen, Phys. Rev. B 88, 220509 (2013).
[27] P.J. Hirschfeld, M.M. Korshunov, and I.I. Mazin, Rep. Prog. Phys. 74, 124508 (2011).