Spin-orbit induced mixed-parity pairing in Sr$_2$RuO$_4$: a quantum many-body calculation

J.J. Deisz* and T.E. Kidd

Department of Physics, University of Northern Iowa, Cedar Falls, Iowa 50614, USA
(Dated: February 17, 2022)

The unusual superconducting state in Sr$_2$RuO$_4$ has long been viewed as being analogous to a superfluid state in liquid $^4$He. Nevertheless, calculations based on this odd-parity state are presently unable to completely reconcile the properties of Sr$_2$RuO$_4$. Using a self-consistent quantum many-body scheme that employs realistic parameters, we are able to model several signature properties of the normal and superconducting states of Sr$_2$RuO$_4$. We find that the dominant component of the model superconducting state is of even parity and closely related to superconducting state for the high-$T_c$ cuprates although a smaller odd-parity component is induced by spin-orbit coupling. This mixed pairing state gives a more complete representation of the complex phenomena measured in Sr$_2$RuO$_4$.

The unusual electronic properties of the layered material Sr$_2$RuO$_4$ remain of significant interest eight years after Mackenzie and Maeno’s review [1] of an already extensive literature. Experiments show a quasi two-dimensional Fermi liquid state for $T < 100$K with an unconventional superconducting state emerging at $T_c = 1.5$K. A qualitative description of the normal state Fermi liquid has emerged through band structure calculations. Three quasiparticle bands, $\alpha$, $\beta$ and $\gamma$, originating from $d_{xz}$, $d_{yz}$, and $d_{xy}$ orbitals of tetragonally-coordinated Ru ions, cross the Fermi surface [2, 3]. The nature of the superconducting state is less well established, but the lack of in-plane Knight shifts for $T < T_c$ [4] and the presence of finite signals in symmetry sensitive probes such as the polar Kerr [5] or the Josephson effects [6, 7] point to spin-triplet, odd-parity pairing and, more specifically, to a chiral pairing state with zero total pair spin perpendicular to the planes, i.e $S_z = 0$. Nonetheless, other experiments are not so well-explained by such a pairing state [8]: the specific heat for $T << T_c$ [9] shows evidence of nodes or minima in the superconducting gap function, but a chiral $p$-wave state is nodeless; the out-of-plane Knight shift [10] is weakly temperature dependent below $T_c$; and edge currents are not detectable at a level that is two orders of magnitude below the expected value [11]. More recently, signatures of half-quantum vortices below $T_c$ were explained in terms of equal spin pairing, i.e. $S_z \neq 0$ [12]. Thus, the nature of the bulk superconducting state is still not resolved completely and it is essential to test current working assumptions with microscopic calculations that are as detailed as possible.

Our calculation starts with a tight-binding representation of an LDA band-structure for Sr$_2$RuO$_4$ as developed by Pavarini and Mazin [13]. Low energy electronic states are represented with a basis consisting of a $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbital for each Ru ion and these are $2/3$ filled on average. Ru ions are strongly coupled within planes where they form a square lattice of side $a = 3.87\AA$. Weak interplanar couplings corresponding to the $z$ direction are ignored. For the Ru atomic spin-orbit interaction, $\lambda \vec{s} \cdot \vec{l}$, we use $\lambda = 70$ meV [14]. The interaction of atomic spin and orbital moments and a uniform external field is given by $-\mu_B (g_s \vec{s} + \vec{l}) \cdot \vec{B}$.

Dynamical correlation effects are modeled on the basis of an atomically local bare interaction with three parameters; $U$ and $U'$ for inter- and intra-orbital Coulomb repulsion and $J$ for interorbital exchange; and the fluctuation exchange approximation (FLEX). Here we will only consider fixed ratios of $U'/U = 2/3$ and $J/U = 1/6$ that are typically used in these calculations [15]; variations in these ratios have little impact on general features of our results. Having fixed the ratios we find that $U < 1$ eV is reasonably consistent with the observed $T_c = 1.5$K, but we will in some instances use a somewhat larger value of $U = 1.2$ eV as the higher $T_c$ that results makes superconducting state calculations more feasible. To make the scheme computationally feasible, the dynamical cluster approximation [16] is used to reduce dynamical correlations to a range of $L_c << L$ where $L \sim 100\mu m$ is the physical lattice dimension and we numerically demonstrate that our results well-describe the large $L_c$ limit. Translationally invariant, but otherwise random initial configurations are used to seed the self-consistent procedure which then terminates when a stable state is produced.

Figure 1 compares the renormalized normal state ($T = 60$K) electronic structure of Sr$_2$RuO$_4$ as determined by FLEX calculations for $U = 0.9$eV with bare band dispersions derived from LDA [13]. The FLEX band dispersions have significantly smaller slopes at the Fermi level than unrenormalized LDA counterparts. These indicate a significant mass enhancement for each band that is expected from specific heat [17] and dHvA [18] measurements. The imaginary part of the self energy for each band is proportional to $(E - \varepsilon_F)^2$ as is expected for a Fermi liquid.

As the calculations can be used to determine the electronic structure with both energy and momentum resolution, it is natural to present a comparison to angle resolved photoemission experiments. Fortunately, once the problem of a surface reconstruction was resolved [19],
Deisz, Figure 1 of 3

![Graph](image_url)

FIG. 1. (Color online) Comparison of low energy band structure derived from FLEX calculations (symbols) and LDA (solid lines) along the indicated symmetry directions. The vertical lines through each point correspond to the inverse lifetime of the state. There is a significant renormalization of each band, with the γ band showing the strongest renormalization along Γ-M.

there have been a plethora of high quality photoemission experiments that probed the bulk normal state electronic structure of Sr$_2$RuO$_4$[20–23]. For the β and γ band crossings along Γ-M, the calculated dynamical renormalizations of the Fermi velocity, $v_F/LDA/v_F/FLEX$ where $v_F = dE/dk|_{k=k_F}$, are 1.9 and 3.4 which compare well to the experimental values of (approximately) 1.7 and 3.3 [22].

A more striking renormalization is the shift of the van Hove singularity in the γ-band at the M point from 90 meV to 20 meV in going from the LDA to FLEX results. This feature is clearly apparent in photoemission experiments utilizing either thermally occupied states or doping [24]. This confirms that FLEX is capturing non-trivial normal-state correlation effects that could be key precursors to the superconducting transition. We note that spin-orbit coupling leads to non-negligible spin and orbital mixing for γ-band quasiparticles at $\epsilon_F$ along Γ-M with that $d_{xz}$ orbitals contributing about 15% of the quasiparticle weight. Since the spin-orbit induced mixing of $d_{xy}$ and $d_{xz}$ orbitals involves a spin flip, i.e. $l^+s^-$, these quasiparticles have a wavefunctions of the form $|\psi^{dp}\rangle \sim c_1|d_{xy},\uparrow\rangle + c_2|d_{xz},\downarrow\rangle$, i.e. they are not pure spin-eigenstates.

Superconductivity is associated with the stability of finite anomalous Green's function amplitudes, $F_{\nu\nu',\sigma}(\vec{R},\tau) \equiv -T_{\tau} c_{\nu\sigma}(\vec{R},\tau)c_{\nu',\sigma}(\vec{R},\tau=0)^\dagger$. As an order parameter amplitude for the superconducting state we take $m^2_p(T) = \sum_{\nu\nu',\sigma}\langle F_{\nu\nu',\sigma}(\vec{R},\tau=0)\rangle^2$ and fit the temperature dependence of $m_p(T)$ to a power-law function, $a_0|T - a_2|^a_1$ to estimate $T_c = a_2$. Results for $T_c$ versus $U$, $\lambda$ and $L_c$ are shown in Table 1. While the numerical parameter $L_c$ does affect quantitative results, qualitative features are reasonably well described with $L_c = 4a$. With spin-orbit coupling $(\lambda = 0.07)$ we find that $T_c \sim 20 - 30K$ for $U=1.2$ eV and $T_c \lesssim 10K$ for $U = 0.9$ eV. Thus, $U \lesssim 0.9$ eV is most consistent with the observed $T_c$, unless the spin-orbit interaction for Sr$_2$RuO$_4$ in actuality is much larger than 0.07 eV. Recall that $U=0.9$ eV leads to quantitative agreement with photoemission results as well.

To examine the spatial, orbital and spin dependence of the pairing state, we define a normalized pair wave function and decompose it into eigenfunctions of total spin, $(S, S_z)$.

$$\Psi^{(S,S_z)}_{\nu\nu'}(\vec{R}) = \frac{1}{m_p} F^{(S,S_z)}_{\nu\nu'}(\vec{R},0) = \sum_{S, S_z} \Psi^{(S,S_z)}_{\nu\nu'}(\vec{R}) \chi^{(S,S_z)}$$

from which we obtain a fractional weight by total spin, $p^{(S,S_z)}$, by taking the complex squares of $\Psi^{(S,S_z)}_{\nu\nu'}(\vec{R})$ and tracing over orbital indices and displacements. In Table 1 we show results for these weights as a function of $U$, $\lambda$ and $L_c$ evaluated at $T \sim T_c$. These results show a pure singlet pairing state when spin-orbit coupling is absent, i.e $\lambda = 0$. Further examination of the orbital and spatial properties of $\Psi^{(0,0)}_{\nu\nu'}(\vec{R})$ show that this singlet state has $d_{xz}$ symmetry with respect to rotations in the plane, i.e. $\Psi^{(0,0)}_{xy-xy}(a\vec{q}) = -\Psi^{(0,0)}_{xy-xy}(a\vec{q})$, and that the only significant orbital contributions come from the $d_{xy}$-orbitals with the very small contributions from $d_{xz}$ and $d_{yz}$ orbitals vanishing completely in the limit $J \to 0$. Consequently, for $\lambda = 0$ we find that the superconducting state

| model parameters | calculated values |
|------------------|-------------------|
| $U$ (eV) | $\lambda$ (eV) | $L_c/a$ | $T_c$ (K) | $p^{(0,0)}$ | $p^{(1,1)}$ | $p^{(1,0)}$ | $p^{(1,-1)}$ |
| 1.2 | 0.00 | 4 | 39 | 1.0 | 0 | 0 | 0 |
| 1.2 | 0.00 | 8 | 29 | 1.0 | 0 | 0 | 0 |
| 1.2 | 0.02 | 4 | 39 | 0.986 | 0.0070 | 0.000021 | 0.0070 |
| 1.2 | 0.07 | 4 | 35 | 0.848 | 0.075 | 0.0019 | 0.075 |
| 1.2 | 0.07 | 8 | 22 | 0.785 | 0.106 | 0.0018 | 0.106 |
| 1.2 | 0.07 | 16 | 29 | 0.795 | 0.101 | 0.0021 | 0.101 |
| 0.9 | 0.00 | 4 | 15 | 1.0 | 0 | 0 | 0 |
| 0.9 | 0.07 | 4 | 6 | 0.762 | 0.118 | 0.0023 | 0.118 |
| 0.9 | 0.07 | 8 | 6 | 0.713 | 0.142 | 0.0017 | 0.142 |

Table 1. The transition temperature, $T_c$, and pair wave function weights by spin, $p^{(S,S_z)}$, as a function of the Coulomb repulsion strength ($U$), and spin-orbit coupling constant ($\lambda$) and dynamical cluster size ($L_c$). In the absence of spin-orbit coupling ($\lambda = 0$), the pairing state is a pure singlet. Spin-orbit coupling induces triplet components to the pairing state, primarily between electrons with equal $z$-components of spin, $S_z = \pm 1$.
leaves the $\alpha$ and $\beta$ bands ungapped or very nearly so and the $\gamma$-band gap has nodes typical of a $d_{x^2-y^2}$ pairing state.

A finite spin-orbit coupling constant, $\lambda \neq 0$, finite triplet pairing components. The largest amplitudes for triplet pairing occur for equal spin pairs, i.e. $S_z = \pm 1$. Further examination of the wavefunctions for $S_z = \pm 1$ reveals that they describe interorbital pairing between an electron in the $d_{xy}$ orbital and an electron in either of the $d_{xz}$ or $d_{yz}$ orbitals. Also we find $\pm\pi/2$ phase shifts between the two types of interorbital terms in this wavefunction with opposite relative signs for the up and down spin pairs, i.e. $\Psi_{x,y,yz}(a\hat{y}) = e^{-i\pi/2}\Psi_{x,y,xz}(a\hat{x})$ and $\Psi_{x,y,yz}^{(1,-1)}(a\hat{y}) = e^{+i\pi/2}\Psi_{x,y,xz}^{(1,-1)}(a\hat{x})$. Odd-parity states of this form are "topological," time-reversal invariant superconducting states and their unique properties have recently been described by Qi, et al. [25]. Tada et al. [26] have performed model calculations that point to the possibility of generating such a state at the interface via spin-orbit coupling although they suggest that weaker spin-orbit effects lead to a chiral $p$-wave state in the bulk. Note that for such a state up and down spin equal-spin pairs have opposite chirality, so no net charge current is expected on the edges, a result that is consistent with experiment [11]. We note that for fixed values of $U$ and $\lambda$, the relative contribution of singlet and triplet pairing terms is weakly dependent on the numerical parameter $L_c$ with little change observed in going from $L_c/a = 8$ to 16.

In Figure 2, we show the quasiparticle excitation spectrum for $T \sim 0.5T_c$ along the $\Gamma$-M cut evaluated with $U = 1.2$ eV and $L_c = 4a$ as a function of reduced temperature, $T/T_c$, are displayed in Figure 3. For $\lambda = 0$ we find that $\chi_{xx} = \chi_{zz}$ is suppressed by about 1/3 below $T_c$, but the curves do not approach zero as $T \to 0$ as the $\alpha$-band and $\beta$-band Fermi surfaces remain ungapped. In the mixed pairing state, for $\lambda = 0.07$ eV, $\chi_{xx}$ and $\chi_{zz}$ are no longer equal, but each has a weak temperature dependence below $T_c$ with changes of less than 10% compared to $T \sim T_c$. Thus, the qualitative behavior of the temperature-dependent spin susceptibility for this mixed pairing state apparently is in good agreement with Knight shift data. Further, these results suggest that the small Knight shifts in Sr$_2$RuO$_4$ are caused by the mixed-spin nature of quasiparticle states, a general mechanism for small Knight shifts described by Anderson [27], and not by a bulk $p$-wave symmetry pairing state.

![Deisz, Figure 2 of 3](image1)

**FIG. 2.** Quasiparticle spectrum along the $\Gamma$-M direction for $T < T_c$. The usual signature of a superconducting gap appears in the $\gamma$-band. There is no evidence for a smaller gap forming in the $\beta$-band along this cut to within the momentum resolution of the calculation.

![Deisz, Figure 3 of 3](image2)

**FIG. 3.** Temperature dependence of the Pauli spin susceptibility, $\chi_{sp}$, for zero and finite spin-orbit coupling constant, $\lambda$. For $\lambda = 0$ the equal in-plane and out-of-plane components are suppressed by the superconducting transition In contrast, for $\lambda = 70$ meV, both the in-plane and out-of-plane components are suppressed by less than 10% for $T < T_c$.

We note, though, that the overall scale for the calcu-
lated susceptibilities are a factor of about four too small in comparison to experiment [17]. The lack of quantitative accuracy in this instance is most likely a failure of FLEX as the approximation has been shown to underestimate the large enhancements of the magnetic susceptibility that are expected in the vicinity of a magnetic phase transition for the special case of the single-band Hubbard model [28].

Thus, the mixed pairing superconducting state is consistent with major experimental features of Sr$_2$RuO$_4$ in both the superconducting and normal states. However, the time-reversal symmetry preserving nature of this mixed-parity state places these results at odds with the interpretation of polar Kerr and tunneling experiments [5, 7]. We note that such an interpretation of the tunneling data requires the presence of superconducting domains of size $\lesssim 1 \mu$m, which is too small to account for a finite signal in the infrared frequencies used in the polar Kerr effect experiments [8]. Also the existence of a finite polar Kerr effect at the pseudogap temperature, $T^*$, in the cuprate superconductors suggests that this probe is sensitive to correlations other than those directly related to a time-reversal symmetry breaking superconducting state [29]. It remains to be seen whether the correlation between experiment and calculations can be improved by accounting for additional details such as vortices, defects, impurities, surface effects, domains and other perturbations, all of which have been found to be necessary for enabling the theory for a pure $p$-wave superconducting ground state to be consistent with the wide range of experimental studies of the system.

The results shown here are supported by earlier theoretical work. For example, Kuwabara and Ogata [30] showed that fluctuations may favor a $d_{x^2-y^2}$ pairing given certain parameters in an effective one-band model for Sr$_2$RuO$_4$. In the course of developing a theory for a $p$-wave superconducting state for Sr$_2$RuO$_4$, it has long been understood that spin-orbit coupling might play a role in stabilizing one of the possible $p$-wave pairing states [14], but less attention has been placed on the impact of spin-orbit coupling on a nominally $d_{x^2-y^2}$ pairing state. However, at the conclusion of their study of spin-orbit effects on the band structure of Sr$_2$RuO$_4$ and Sr$_2$RhO$_4$, Haverkort, et al. state “In fact, singlet and triplet states could be mixed, blurring the distinction between spin-singlet and spin triplet-pairing ... [31].” Indeed, we find that when dynamical correlations and spin-orbit interactions are simultaneously taken into account using realistic parameters for Sr$_2$RuO$_4$ such a mixed-parity bulk state is realized. As FLEX is an approximate many-body scheme its identification of the superconducting state for the underlying three-band model must be considered tentative until it is computationally feasible to include terms that are missing in FLEX (i.e. vertex corrections in the self-energy series) or perform a quantum Monte Carlo analysis. Nonetheless, this FLEX analysis represents a methodological step forward as it incorporates physical effects not included in earlier finite-order perturbative studies [32, 33], namely (i) collective spin fluctuations via an infinite set of ladder diagrams and (ii) dynamical quasiparticle renormalizations via self-consistency of the electron Greens function. As these effects are not small, it is unsurprising that a different conclusion results with respect to the pairing symmetry.

T.E.K acknowledges support from the Iowa Office of Energy Independence Award No. 09-IPF-11. J.J.D. as supported in part by a Professional Development Assignment from the University of Northern Iowa. J.J.D. thanks Paul Gray of the University of Northern Iowa for computational support and R.R.P. Singh and the Physics Department of the University of California, Davis for hosting him and many useful conversations during the time this work was initiated.

* john.deisz@uni.edu

[1] A. P. Mackenzie and Y. Maeno, Rev. Mod. Phys., 75, 657 (2003).
[2] T. Oguchi, Phys. Rev. B, 51, 1385 (1995).
[3] A. P. Mackenzie, S. R. Julian, A. J. Diver, G. G. Louzarich, N. E. Hussey, Y. Maeno, S. Nishizaki, and T. Fujita, Physica C: Superconductivity, 263, 510 (1996), ISSN 0921-4534, proceedings of the International Symposium on Frontiers of High-Tc Superconductivity.
[4] K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z. Mao, and Y. Maeno, Nature, 396, 658 (1998).
[5] J. Xia, Y. Maeno, P. T. Beyersdorf, M. M. Fejer, and A. Kapitulnik, Phys. Rev. Lett., 97, 167002 (2006).
[6] K. D. Nelson, Z. Q. Mao, Y. Maeno, and Y. Liu, Science, 306, 1151 (2004), http://www.sciencemag.org/content/306/5699/1151.full.pdf.
[7] F. Kidwingira, J. D. Strand, D. J. Van Harlingen, and Y. Maeno, Science, 314, 1267 (2006), http://www.sciencemag.org/content/314/5803/1267.full.pdf.
[8] C. Kallin and A. J. Berlinsky, Journal of Physics: Condensed Matter, 21, 164210 (2009).
[9] S. Nishizaki, Y. Maeno, and Z. Mao, Journal of Low Temperature Physics, 117, 1581 (1999), ISSN 0022-2291, 10.1023/A:1022551313401.
[10] H. Murakawa, K. Ishida, K. Kitagawa, Z. Q. Mao, and Y. Maeno, Phys. Rev. Lett., 93, 167004 (2004).
[11] J. R. Kirtley, C. Kallin, C. W. Hicks, E.-A. Kim, Y. Liu, K. A. Moler, Y. Maeno, and K. D. Nelson, Phys. Rev. B, 76, 014526 (2007).
[12] J. Jang, D. G. Ferguson, V. Valaryuk, R. Budakian, S. B. Chung, P. M. Goldbart, and Y. Maeno, Science, 331, 186 (2011), http://www.sciencemag.org/content/331/6014/186.full.pdf.
[13] E. Pavarini and I. I. Mazin, Phys. Rev. B, 74, 035115 (2006).
[14] K. K. Ng and M. Sigrist, EPL (Europhysics Letters), 49, 473 (2000).
[15] J. Mravlje, M. Aichhorn, T. Miyake, K. Haule, G. Kotliar, and A. Georges, Phys. Rev. Lett., 106, 096401 (2011).
[16] M. H. Hettler, A. N. Tahvildar-Zadeh, M. Jarrell, T. Pruschke, and H. R. Krishnamurthy, Phys. Rev. B, 58, R7475 (1998).

[17] Y. Maeno, K. Yoshida, H. Hashimoto, S. Nishizaki, S. Ikeda, M. Nohara, T. Fujita, A. Mackenzie, N. Hussey, J. Bednorz, and F. Lichtenberg, Journal of the Physical Society of Japan, 66, 1405 (1997).

[18] C. Bergemann, J. S. Brooks, L. Balicas, A. P. Mackenzie, S. R. Julian, Z. Q. Mao, and Y. Maeno, Physica B: Condensed Matter, 294-295, 371 (2001), ISSN 0921-4526.

[19] A. Damascelli, D. H. Lu, K. M. Shen, N. P. Armitage, F. Ronning, D. L. Feng, C. Kim, Z.-X. Shen, T. Kimura, Y. Tokura, Z. Q. Mao, and Y. Maeno, Phys. Rev. Lett., 85, 5194 (2000).

[20] N. J. C. Ingle, K. M. Shen, F. Baumberger, W. Meevasana, D. H. Lu, Z.-X. Shen, A. Damascelli, S. Nakatsuji, Z. Q. Mao, Y. Maeno, T. Kimura, and Y. Tokura, Phys. Rev. B, 72, 205114 (2005).

[21] T. E. Kidd, T. Valla, A. V. Fedorov, P. D. Johnson, R. J. Cava, and M. K. Haus, Phys. Rev. Lett., 94, 107003 (2005).

[22] H. Iwasawa, Y. Aiura, T. Saitoh, I. Hase, S. I. Ikeda, Y. Yoshida, H. Bando, M. Higashiguchi, Y. Miura, X. Y. Cui, K. Shimada, H. Namatame, and M. Taniguchi, Phys. Rev. B, 72, 104514 (2005).

[23] Y. Aiura, Y. Yoshida, I. Hase, S. I. Ikeda, M. Higashiguchi, X. Y. Cui, K. Shimada, H. Namatame, M. Taniguchi, and H. Bando, Phys. Rev. Lett., 93, 117005 (2004).

[24] K. M. Shen, N. Kikugawa, C. Bergemann, L. Balicas, F. Baumberger, W. Meevasana, N. J. C. Ingle, Y. Maeno, Z.-X. Shen, and A. P. Mackenzie, Phys. Rev. Lett., 99, 187001 (2007).

[25] X.-L. Qi, T. L. Hughes, S. Raghu, and S.-C. Zhang, Phys. Rev. Lett., 102, 187001 (2009).

[26] Y. Tada, N. Kawakami, and S. Fujimoto, New Journal of Physics, 11, 055070 (2009).

[27] P. W. Anderson, Phys. Rev. Lett., 3, 325 (1959).

[28] N. E. Bickers and S. R. White, Phys. Rev. B, 43, 8044 (1991).

[29] R.-H. He, M. Hashimoto, H. Karapetyan, J. D. Koralek, J. P. Hinton, J. P. Testaud, V. Nathan, Y. Yoshida, H. Yao, K. Tanaka, W. Meevasana, R. G. Moore, D. H. Lu, S.-K. Mo, M. Ishikado, H. Eisaki, Z. Hussain, T. P. Devereaux, S. A. Kivelson, J. Orenstein, A. Kapitulnik, and Z.-X. Shen, Science, 331, 1579 (2011), http://www.sciencemag.org/content/331/6024/1579.full.pdf.

[30] T. Kuwabara and M. Ogata, Phys. Rev. Lett., 85, 4586 (2000).

[31] M. W. Haverkort, I. S. Elfimov, L. H. Tjeng, G. A. Sawatzky, and A. Damascelli, Phys. Rev. Lett., 101, 026406 (2008).

[32] T. Nomura and K. Yamada, Journal of the Physical Society of Japan, 69, 3678 (2000).

[33] Y. Yanase and M. Ogata, Journal of the Physical Society of Japan, 72, 673 (2003).