

# Interpretation of the Isomeric Chemical Shifts in Au<sup>197†\*</sup>

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The large chemical shifts recently observed in Mössbauer absorption experiments on Au<sup>197</sup> are explained on the basis of Coulombic interaction between the 6s electron of gold and the 3s<sub>1/2</sub> and 2d<sub>3/2</sub> protons. A first-order perturbation calculation is made, using the Coulombic potential within the nucleus due to the 6s electron. Proton wave functions derived from harmonic-oscillator, square-well, and Woods-Saxon nuclear potentials are treated. The latter two potentials yield results that are in reasonable accord with experiment. This model can afford a sensitive comparison of nuclear potentials as well as a determination of the s conduction-electron density on impurity atoms. In particular, this calculation discriminates against the harmonic-oscillator potential and shows that the 6s electron density on a gold impurity atom in several hosts is higher than in pure gold. These results also indicate that the 3s<sub>1/2</sub> proton subshell is filled in the ground state of Au<sup>197</sup>.

## I. INTRODUCTION

RECENT observations of shifts due to environmental effects in the isomeric energy-level spacing of nuclei<sup>1</sup> show promise of leading to new techniques for studying certain chemical effects in solids, as well as providing more insight into some of the mechanisms responsible for isotope shifts. Until now, these chemical shifts<sup>2</sup> have been interpreted as being proportional to the product of a difference, for different environments, in the average electron density at the nucleus times a difference in the mean-square charge radii of the two isomeric nuclear states.<sup>3,4</sup> For most of the nuclei investigated (which have an even number of protons), this difference in charge radius is difficult to interpret in detail, and it is not clear how the interpretation should be refined. Recently, however, data have been obtained on the isomeric chemical shift of the resonant 77-keV transition in Au<sup>197</sup>, an odd-proton nucleus.<sup>5-7</sup> In this case the first excited state may be associated with proton excitation, and a change in the mean-square charge radius may be interpreted in terms of the proton wave functions. In this paper we present a detailed calculation, based on this model, of the isomeric chemical shifts expected in Au<sup>197</sup>.

## II. OUTLINE OF THE PROBLEM

The basic hypothesis here, as for the isotope shift, is that the effect is Coulombic in origin. Thus we may

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<sup>1</sup> O. C. Kistner and A. W. Sunyar, *Phys. Rev. Letters* **4**, 412 (1960).

<sup>2</sup> We prefer the term "chemical shift," or possibly "isomeric chemical shift," over "isomer shift" because it conveys more information about the origin of the shift, as well as following the tradition of naming shifts for their unobserved variables (e.g., the isotope shift in optical spectroscopy).

<sup>3</sup> S. DeBenedetti, G. Lang, and R. Ingalls, *Phys. Rev. Letters* **6**, 60 (1961).

<sup>4</sup> L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

<sup>5</sup> L. D. Roberts and J. O. Thomson, *Bull. Am. Phys. Soc.* **6**, 75 (1961).

<sup>6</sup> D. A. Shirley, M. Kaplan, and P. Axel, *Phys. Rev.* **123**, 816 (1961).

<sup>7</sup> L. D. Roberts and J. O. Thomson, *Bull. Am. Phys. Soc.* **6**, 230 (1961).

determine the electron density  $\rho(r)$  within and near the nucleus and do a first-order perturbation calculation using appropriate nuclear wave functions and the perturbation energy

$$V(r) = -\frac{e^2}{4\pi\epsilon_0} \int_0^r \frac{\rho(r') dr'}{r}. \quad (1)$$

We choose the above convenient limits of integration because we are interested only in differences between the Coulombic interactions of the two isomeric states. Ideally, complete nuclear wave functions would be used for the two states. Lacking these, we assume that the nucleus participates in the shift primarily through the odd proton or hole. This proton (hole) is then described by the 3s<sub>1/2</sub> (excited state) and 2d<sub>3/2</sub> (ground state) shell-model wave functions. We note that, inasmuch as the excited state is assumed to be formed from the ground state by excitation of a single particle, and the shift-producing potential is spherically symmetrical, the modes of coupling within proton subshells in the two states do not affect the result.

The populations of the subshells, however, can be important if the excited state is formed by breaking a pair, exciting one proton of the broken pair to the subshell containing the odd proton, and pairing it with this odd proton. Thus, if the ground state has the configuration  $(h_{11/2})^{10}(s_{1/2})^2(d_{3/2})^3$  and the excited state is  $(h_{11/2})^{10}(s_{1/2})(d_{3/2})^4$ , the isomeric shift will have the same magnitude but the opposite sign from that to be expected if the ground state were  $(h_{11/2})^{12}(d_{3/2})^3$  and the excited state  $(h_{11/2})^{12}(d_{3/2})^2(s_{1/2})$ . The former set of configurations has been favored by Zeldes on the basis of shell-model systematics,<sup>8</sup> but careful consideration of pairing forces probably will modify his conclusions. At least it seems clear that the  $h_{11/2}$  subshell lies sufficiently far below the Fermi surface so that its population will not change appreciably between the isomeric states,<sup>9</sup> and we are thus on fairly safe ground in considering only the 3s<sub>1/2</sub> and 2d<sub>3/2</sub> states. A complete interpretation of chemical-shift data should allow us to distinguish between these

<sup>8</sup> N. Zeldes, *Nuclear Phys.* **2**, 1 (1956/57).

<sup>9</sup> S. G. Nilsson, Lawrence Radiation Laboratory, Livermore, California (private communication).

possible nuclear configurations. The above configurations suggested by Zeldes are used in the following calculation to derive the expected sign of the shifts. Independent experimental and theoretical support for this choice is discussed in Sec. V.

To evaluate  $V(r)$  in Eq. (1), we must decide which electronic states of gold are important in the chemical shift. The requirements are (a) the electron must have a substantial probability density at the nucleus, and (b) this density must be subject to change when the environment of the gold atom is changed (i.e., the electron must participate in a chemical bond, go into a conduction band, etc.). Only the 6s electron seems to meet both requirements to an important extent, and our calculations will involve only this electron. We shall, in fact, use the wave function of a 6s electron on a free gold atom to evaluate the 6s electron density. Near the nucleus, this wave function should be quite similar to that of a 6s electron in metallic gold, both in functional behavior and in magnitude.

The distribution of the electron density inside the nucleus depends on the total nuclear-charge distribution, which we have assumed to be uniform in our calculation. The actual nuclear-charge distribution is probably not far from uniform,<sup>10</sup> and the electron-density distribution is not particularly sensitive to small variation in this quantity.<sup>11,12</sup>

With these approximations, the problem becomes one of calculating the Coulomb interaction between the 6s electron of gold and the odd proton or hole. We might expect, then, that if the proton states are properly described by the nuclear wave functions which we use, the total range of all the experimental chemical shifts will correspond to a change of one 6s electron or less on the gold atom. We shall use this as the first criterion for a reasonable answer, and experimental results may be interpreted in terms of the ratio of the experimental shift to the shift calculated for the addition of one 6s electron to the gold atom (i.e., in terms of the number of 6s electrons added or removed).

### III. THE ELECTRONIC COULOMB POTENTIAL

Before discussing the details of this calculation, we mention an alternative approach which has been used in interpreting the isotope shift. In this approach one assumes that the nucleus is a uniformly charged sphere, or some simple modification thereof.<sup>12,13</sup> Then the shift is equivalent to the optical shift of an *s* electron and is proportional to the product of a mean electron density  $|\psi(0)|^2$  times the difference between the second radial moments of nuclear charge for the two isotopes (isomers). In the relativistic case, the second moment be-

comes the  $2\sigma$ th moment, where  $\sigma = [1 - (\alpha Z)^2]^{\frac{1}{2}}$ .<sup>14</sup> With this simple interpretation, the relative sizes of the isotopes (isomers) may be deduced from experiment. In the absence of other information about the configurations of the nuclear states, a more detailed interpretation is unnecessary.

Evaluation of the Coulomb potential is straightforward, involving only the substitution of the 6s electron density into Eq. (1). Fortunately, in the case of gold, enough data are available to determine the electron density accurately.<sup>15,16</sup> Substituting these into the expression<sup>17</sup>

$$\hbar\Delta\nu = -\frac{4}{3}\pi g_I g_J \mu_0^2 |\psi(0)|^2 (2I+1), \quad (2)$$

we obtain  $|\psi(0)|^2 = 2.67 \times 10^{26} \text{ cm}^{-3}$  for the average 6s electron density inside the nucleus. The density distribution within the nucleus may be obtained from the formulas of Bohr and Weisskopf,<sup>18</sup> normalized to this average density, giving, in terms in  $r^4$ ,

$$|\psi(x)|^2 = (2.91 \times 10^{26})(1 - 0.1666x^2 + 0.0363x^4), \quad (3)$$

with  $x=r/R$ , where  $R$  is the nuclear radius, taken as  $7.00 \times 10^{-13} \text{ cm}$  in this paper. The external electron density approaches the power dependence for a point nucleus given by Racah<sup>19</sup> somewhat outside the nucleus,  $|\psi(r)|^2 \propto r^{2\sigma-2}$  ( $=r^{-0.36}$  for gold). Immediately outside the nucleus, the electron density is obtained by matching to the internal solutions the components,  $f$  and  $g$ , of the Dirac wave function for the 6s electron. This has been done explicitly by Meligy,<sup>20</sup> who has given approximate solutions that have the form

$$\begin{aligned} f &= Ax^\sigma + Bx^{-\sigma}, \\ g &= Cx^\sigma + Dx^{-\sigma}, \end{aligned} \quad (4)$$

as well as exact solutions, immediately outside the nucleus. Determining  $A$ ,  $B$ ,  $C$ , and  $D$  in Eq. (4) by matching  $f$  and  $g$  and their derivatives to the internal solutions at the nuclear surface, we obtain for the electron density in the region immediately outside the nucleus,

$$|\psi(x)|^2 = 2.91 \times 10^{26} [0.971x^{2\sigma-2} + 0.008x^{-2\sigma-2} - 0.109x^{-2}] \text{ cm}^{-3}, \quad (5)$$

with  $x > 1$ . From Eqs. (1), (3), and (5), the expression for the perturbing Coulomb potential becomes

$$V(x) = 2.58 \times 10^{-4} [0.1666x^2 - 0.0083x^4 + 0.0009x^6] \text{ ev} \quad (6a)$$

<sup>14</sup> We are grateful to L. R. Walker, Bell Telephone Laboratories, Murray Hill, New Jersey, for pointing out this method.

<sup>15</sup> H. H. Woodbury and G. W. Ludwig, *Phys. Rev.* **117**, 1287 (1960).

<sup>16</sup> G. Fricke, S. Penselm, and E. Recknagel, *Naturwissenschaften* **48**, 129 (1960).

<sup>17</sup> W. A. Nierenberg, *Ann. Rev. Nuclear Sci.* **7**, 357 (1957).

<sup>18</sup> A. Bohr and V. F. Weisskopf, *Phys. Rev.* **77**, 94 (1950).

<sup>19</sup> G. Racah, *Nature* **129**, 723 (1932).

<sup>20</sup> A. S. Meligy, *Nuclear Phys.* **14**, 248 (1959/60).

<sup>10</sup> See, for example, A. A. Ross, H. Mark, and R. D. Lawson, *Phys. Rev.* **102**, 1613 (1956).

<sup>11</sup> S. G. Nilsson and J. O. Rasmussen, *Nuclear Phys.* **5**, 617 (1958).

<sup>12</sup> A. R. Bodmer, *Nuclear Phys.* **9**, 371 (1958/59).

<sup>13</sup> A. R. Rodmer, *Nuclear Phys.* **21**, 347 (1961).

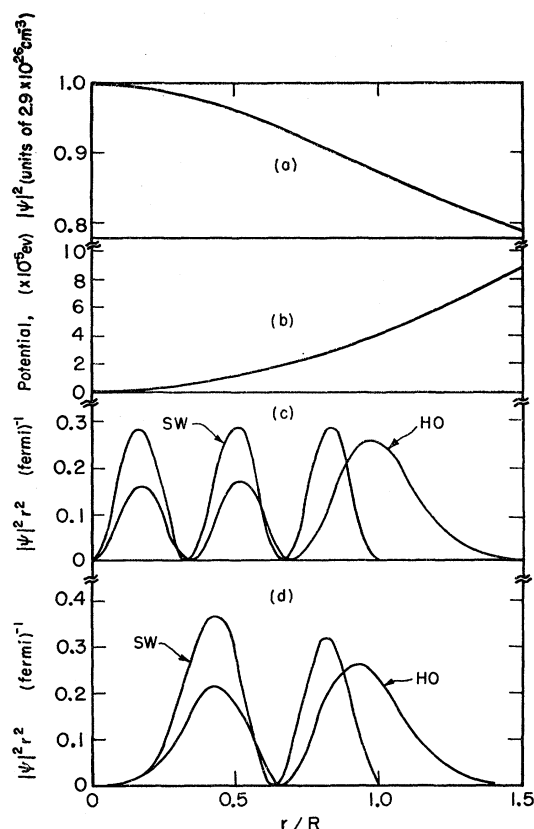


FIG. 1. Plots for  $\text{Au}^{197}$  of (a) the  $6s$  electron density, from Eqs. (3) and (5); (b) the Coulombic potential created by the  $6s$  electron, using Eq. (6a) only [if Eq. (6b) is used in the region  $r > R$ , the potential curve drops off as  $r$  increases, but is only  $2 \times 10^{-6}$  ev lower at  $r = 1.5R$ ]; (c) and (d) the proton distribution for the  $3s_{1/2}$  and  $2d_{3/2}$  states, respectively, using harmonic-oscillator and infinite square-well wave functions.

for  $x < 1$ , and

$$V(x) = 10^{-4}[-1.278 + 0.486x^{2\sigma} + 0.0040x^{-2\sigma}] \text{ ev} \quad (6b)$$

for  $x > 1$ .

Plots of  $|\psi(x)|^2$  and  $V(x)$  are shown in Fig. 1, (a) and (b). Relativity has the important effect of increasing the over-all magnitude of the electron density and the less important effect of changing the shape of the electronic Coulomb potential in and near the nucleus by causing the electron density to be nonuniform. If the density were uniform, only the first term in Eq. (6a) would be nonzero, and this equation would reduce to the mean-square charge-radius approximation.

From Eqs. (6a) and (6b), the chemical shift for the removal of one  $6s$  electron becomes

$$\Delta E = \Delta E_{<} + \Delta E_{>}, \quad (7a)$$

with

$$\Delta E_{<} = 2.58 \times 10^{-4} [0.1666\Delta\langle x^2 \rangle - 0.0083\Delta\langle x^4 \rangle + 0.0009\Delta\langle x^6 \rangle] \text{ ev} \quad (7b)$$

for  $x < 1$ , and

$$\Delta E_{>} = 10^{-4} [0.486\Delta\langle x^{2\sigma} \rangle + 0.0040\Delta\langle x^{-2\sigma} \rangle] \text{ ev} \quad (7c)$$

for  $x > 1$ .

#### IV. NUCLEAR WAVE FUNCTIONS

The choice of nuclear radial wave functions used to evaluate Eq. (6) is rather critical here because of the shape of the perturbing Coulomb potential caused by the  $6s$  electron, which changes considerably in the region  $r \sim R$ . This is just the region where the nuclear potential used in obtaining nuclear wave functions most seriously influences the nucleon density. Thus, for example, a diffuse nuclear potential would allow a substantial probability for the nucleon in question to be in the region  $r > R$ , where the Coulomb interaction with the  $6s$  electron is smaller. For an infinite square-well potential, on the other hand, only the region  $r < R$  would be important, and the chemical shift might be quite different. The calculated chemical shift is shown below to depend sensitively on the diffuseness of the nuclear potential assumed. Thus if the rest of the problem can be understood, chemical shifts can be useful in studying nuclear potentials.

The chemical shift was first calculated using nuclear wave functions derived from a finite square-well potential, for which Eisinger and Jaccarino have calculated the second and fourth radial moments.<sup>21</sup> The contribution to the shift of that part of the proton wave function which is in the region  $r > R$  can easily be shown to be negligible, and only Eq. (5a) need be used in evaluating the shift. Thus the answer is essentially identical to that which would be obtained by using an infinite square-well potential, and may be regarded as characteristic of one limit of nuclear potential "diffuseness." The shift for this potential is  $+2.75 \times 10^{-6}$  ev per  $6s$  electron. The positive sign indicates that the Coulomb interaction with the  $6s$  electron increases the energy difference between the nuclear excited state and ground state.

The shift was also calculated for a three-dimensional isotropic harmonic-oscillator nuclear potential, for which analytical wave functions are available. This is a rather diffuse potential, and may be regarded as the opposite limit to the square-well potential in this respect. As one would expect, the contributions of the external portions of the nuclear wave functions are by no means negligible here. Thus we are not strictly justified in integrating radial moments to infinity using only Eq. (6a), but should use Eq. (6b) in the region  $r > R$ . In fact, we have calculated the shift both ways and the difference in  $\Delta E$  is only about  $1.5 \times 10^{-9}$  ev per  $6s$  electron. This may be understood by observing that, while the proton has only about 75% probability of being in the region  $r < R$ , it has 99.9% probability of

<sup>21</sup> J. Eisinger and V. Jaccarino, *Revs. Modern Phys.* **30**, 528 (1958).

being in the region  $r < 1.5R$ , where Eq. (6a) is still quite accurate. We might generalize this result to conclude that for gold and elements of lower atomic number and for harmonic-oscillator and less diffuse nuclear potentials, it is a good approximation for chemical-shift calculations to use the internal potential and integrate to infinity. Of course, this simplifies these calculations considerably. On the other hand, care must be taken in deriving mean-square charge radii directly from chemical shift data. Such an approximation would be especially poor here, because the two states are derived from the same oscillator shell and we have  $\Delta\langle r^2 \rangle = 0$ . If we use Eq. (6a) and integrate to infinity, the first non-zero contribution to  $\Delta E$  is from the term in  $\langle r^4 \rangle$ . Using an oscillator constant  $\hbar\omega = 41A^{-\frac{1}{2}}$  Mev, we obtain a chemical shift of  $+0.07 \times 10^{-6}$  ev per 6s electron.

Finally, we have evaluated the expected chemical shift using radial wave functions derived from a "realistic" nuclear potential. Blomquist and Wahlborn have calculated radial wave functions for shell-model states in the lead region using a Woods-Saxon diffuse potential.<sup>22</sup> We have scaled their  $3s_{\frac{1}{2}}$  and  $2d_{\frac{3}{2}}$  proton radial functions down to a nuclear radius of 7.00 f and evaluated the second and fourth radial moments by graphical integration. The results are  $\langle x^2 \rangle_s = 0.487$ ,  $\langle x^2 \rangle_d = 0.503$ ,  $\langle x^4 \rangle_s = 0.397$ , and  $\langle x^4 \rangle_d = 0.370$ . The expected shift was evaluated, as discussed above, by combining these values with Eq. (7b), which is again equivalent to integrating to infinity in evaluating the moments in Eq. (7b). This procedure is certainly justified in this case, because the Woods-Saxon potential is considerably less diffuse than the harmonic-oscillator potential, and the proton wave functions fall off somewhat faster outside the nucleus. The relative probability densities from these latter wave functions are shown in Fig. 1, (c) and (d). The shift calculated for proton wave functions based on the Woods-Saxon potential is  $+0.75 \times 10^{-6}$  ev per 6s electron, intermediate between the harmonic-oscillator and square-well results.

## V. DISCUSSION

The calculated shifts are compared with experimental results in Table I. From the experimental shifts and the predicted shifts for the addition of one 6s electron, the fraction of one 6s electron added to or removed from the gold atom in several hosts has been calculated for each of the nuclear potentials considered. Perhaps the most striking feature is the sensitive dependence of the answers obtained on the nuclear potential used in the calculation. In similar calculations on optical isomeric shifts in Au<sup>197</sup>, Weiner did not find this sensitivity.<sup>23</sup> Presumably we found it because we dealt with a case in which the isomeric states are more nearly alike, being derived from the same oscillator level, and the small

TABLE I. Experimental chemical shifts and derived changes in 6s electron density on a gold atom in several hosts, relative to a gold lattice, using several nuclear potentials.

Host	Observed <sup>a</sup> shift (10 <sup>-6</sup> ev)	Number of 6s electrons gained by gold atom		
		Harmonic-oscillator potential	Finite square-well potential	Woods-Saxon potential
Pt	0.26 ± 0.06	4	0.09	0.3
Fe	1.42 ± 0.09	20	0.52	1.9
Co	1.23 ± 0.08	18	0.45	1.6
Ni	1.11 ± 0.08	16	0.40	1.5

differences in radial moments are therefore more sensitive to details of the nuclear potential.

There is strong, though not overwhelming, evidence that the 6s electron density on a gold atom is *higher* when it is in any of the other hosts than in a gold lattice (clearly the density is either higher or lower in *all* the other hosts because all the shifts are positive relative to a gold absorber). Zeldes' shell model calculations indicate that the  $3s_{\frac{1}{2}}$  proton subshell is filled in the ground state of Au<sup>197</sup>. Combining this result with the present work yields the sign of the change in electron density given in Table I. There are two other pieces of evidence, which independently give the same sign. First, a calculation by Blatt and Elliott,<sup>24</sup> using an impurity model similar to Daniel's,<sup>25</sup> suggests that the electron density of gold in iron should be higher than that of gold in gold. Second, the chemical shift of Au<sup>197</sup> in tin is positive,<sup>26</sup> and tin, with a valence of four, almost certainly contributes electrons to the gold impurity atoms.<sup>27</sup>

The harmonic-oscillator shift is at least an order of magnitude too low, while the other two potentials give answers that are certainly of the right order of magnitude, corresponding to changes in 6s electron density on the gold atoms of a fraction of one electron. These latter, less diffuse, potentials should be more realistic for a heavy nucleus such as Au<sup>197</sup>, and it is encouraging that they give reasonable results. When independent data on the 6s electron density on gold impurity atoms become available, it will be interesting to compare the results from these latter potentials in a more quantitative way. Such data could be obtained from Knight shift measurements on gold impurity atoms in any of the hosts in Table I.

We estimate that the assumption of uniform total nuclear charge distribution, consideration of only the 6s electron of gold, and errors in the data used in calculating the shifts should produce a cumulative error of less than 20%. While this model is internally quite satisfactorily, it is weakened somewhat by the sizable

<sup>24</sup> R. J. Elliott, Department of Physics, University of California, Berkeley (private communication, March, 1961).

<sup>25</sup> E. Daniel, J. Phys. Chem. Solids **10**, 174 (1959).

<sup>26</sup> R. W. Grant, M. Kaplan, and D. A. Shirley (unpublished data, April, 1961).

<sup>27</sup> We are indebted to W. J. Carr, Jr., for suggesting this experiment.

<sup>22</sup> J. Blomquist and S. Wahlborn, Arkiv Fysik **16**, 565 (1959/60).

<sup>23</sup> Richard Weiner, Phys. Rev. **114**, 256 (1958).

chemical shifts recently reported for  $\text{Fe}^{57}$  and  $\text{Sn}^{119}$ ,<sup>3,4,28</sup> which are *odd-neutron* nuclei and would exhibit no shifts in first order on this model. These shifts constitute an interesting problem for which there is at present no unique simple solution, although several qualitative explanations are available. (For example, an "effective" positive charge on the odd neutron would fit the  $\text{Sn}^{119}$  data quite well. The shift in  $\text{Fe}^{57}$  may be explained by the complexity of the ground state.) As discussed in reference 6, there is little doubt that the single odd proton is the major contributor to the shift in  $\text{Au}^{197}$ . We estimate that this ambiguity contributes an error of 30% or less to our calculation, and the cumulative error should be less than 50%.

## VI. CONCLUSIONS

The chemical shift in  $\text{Au}^{197}$  can be explained at least semiquantitatively on the basis of the interaction of the odd proton with the  $6s$  electron. The differences among the theoretical results obtained using nuclear wave functions derived from three different nuclear potentials suggests that this type of data could possibly be a useful criterion for deciding among nuclear potentials.

The interpretation of chemical-shift data on heavy nuclei in terms of radial moments is complicated some-

what by relativistic effects. These effects render the  $s$ -electron density near the nucleus nonuniform, thereby producing finite contributions from higher radial moments. The internal expansion of the Coulomb potential due to the  $6s$  electron is sufficiently accurate for some distance outside the nucleus that radial moments of the proton distribution may be evaluated by using only the internal potential and integrating to infinity, even for proton distributions obtained from a harmonic-oscillator nuclear potential.

This shift shows promise of providing useful solid-state information, i.e., the conduction electron density at impurity sites. In particular, this analysis establishes the signs and approximate magnitudes of differences in the conduction-electron density at a gold atom in several lattices.

Finally, the sign of the shifts indicates that the ground state of  $\text{Au}^{197}$  is "smaller" or, more exactly, has more  $3s_{\frac{1}{2}}$  protons than the 77-kev state. This supports Zeldes' conclusion that the  $3s_{\frac{1}{2}}$  subshell is filled in the ground state, which is then best approximated by the shell-model configurations  $(h_{11/2})^{10}(3s_{\frac{1}{2}})^2(2d_{\frac{3}{2}})^3$  or  $(h_{11/2})^{12}(3s_{\frac{1}{2}})^2(2d_{\frac{3}{2}})^1$ .

## ACKNOWLEDGMENTS

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<sup>28</sup> A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Phys. Rev. Letters **5**, 553 (1960).