Comment on “Quantitative x-ray photoelectron spectroscopy: Quadrupole effects, shake up, Shirley background, and relative sensitivity factors from a database of true x-ray photoelectron spectra”

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This Comment demonstrates that a comparison analysis by Seah and Gilmore between experimental data on the X-ray photoelectron spectroscopy intensities and theoretical data by Trzhaskovskaya et al. is misleading due to a number of serious errors made by Seah and Gilmore (PRB 73 174113).

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In a recent publication by Seah and Gilmore [1], a comparison analysis is provided between experimental X-ray photoelectron spectroscopy intensities measured at the National Physical Laboratory and theoretical data by Scofield [2, 3] and by Trzhaskovskaya et al. [4, 5]. Seah and Gilmore claim in the abstract that there is “excellent correlation between experimental intensities... and the theoretical intensities involving the dipole approximation using Scofield’s cross sections. Here, more recent calculations for cross sections by Trzhaskovskaya et al. involving quadrupole terms are evaluated and it is shown that their cross sections diverge from the experimental database results by up to a factor of 5”.

Another conclusion in [1] is concerned with the photoionization cross section σ as well as the photoelectron angular distribution parameters β (the dipole parameter), γ, and δ (quadrupole ones) obtained by Scofield [3] for Ne and Ba at the photon energy  k = 3 keV: “If these data are compared with the data of Trzhaskovskaya et al. [4, 5], good agreement is found for β and δ, whereas γ is generally between 1.01 and 1.45 times greater and σ is between 0.44 and 0.94 of these earlier values”. Note that here Seah and Gilmore [1] have given the wrong reference to one of another Scofield’s papers instead of [3].

We contend that the overall comparison and conclusions concerning values of the photoion-
ization cross section $\sigma$ and the photoelectron angular distribution parameters $\beta, \gamma, \text{and} \delta$ presented in our papers [4, 5], are invalid due to serious errors and shortcomings made in [1]:

(i) Calculations by Scofield and by Trzhaskovskaya et al. are compared in [1] for several values of the photon energy $k$, in particular, for the $K_\alpha$ line of magnesium $k = 1.254$ keV and for $k = 3.0$ keV. Photoionization cross sections [2, 3] and the photoelectron angular distribution parameters [3] are presented by Scofield for these values of the PHOTON ENERGY $k$. In our papers [4, 5], we give cross sections and angular parameters for nine values of the PHOTOELECTRON KINETIC ENERGY $E = k - \varepsilon_b$ where $\varepsilon_b$ is the binding energy of the electron. This is pointed out everywhere in the text of the papers from the title to the Section “Explanation of Tables”. Nevertheless Seah and Gilmore [1] determine interpolated values of $\sigma, \beta, \gamma$ and $\delta$ from [4, 5] using photoelectron energies $E$ as though they were photon energies $k$.

(ii) Comparing the photoionization cross sections for an open atomic subshell, one should take into consideration that values of $\sigma$ are given in [4, 5, 6, 7] for the completely filled subshells even though a subshell is an open one. This is always pointed out in Section “Explanation of Tables” of the papers. In contrast, Scofield [2] has not clearly indicated the manner in which cross sections for the open relativistic doublet subshells have been obtained. However analysis of the $\sigma$ values from [2] lead to the suggestion that he has calculated a combined photoionization cross section $\sigma_{n\ell}$ per a real number of electrons in two subshells with total momenta $j_1 = \ell - 1/2$ and $j_2 = \ell + 1/2$ where $n$ is the principal quantum number and $\ell$ is the orbital momentum. Then $\sigma_{n\ell}$ has been spread between the two relativistic subshells in accordance with their approximate statistical weights.

Because of this, the only comparison of $\sigma_{n\ell} = \sigma_{n\ell j_1} + \sigma_{n\ell j_2}$ for a specific number of electrons is meaningful. This fact is disregarded in [1]. For the open subshell, Seah and Gilmore compare $\sigma_{n\ell j}(S)$ of Scofield for a real number of electrons as mentioned above, with $\sigma_{n\ell j}(T)$ given in our tables [4, 5, 7] for the completely filled subshell, $\sigma_{n\ell j}(T)$ being found mistakenly (see point (i)).

(iii) Besides, it is necessary to bear in mind that different theoretical assumptions may give rise to a difference in the results obtained. In specific cases, the difference may be of great importance. In the comparison of results of the two calculations, Seah and Gilmore do not consider the difference in models used by Scofield and by Trzhaskovskaya et al. [4, 5].

Scofield has assumed the electrons in the initial and final states treated as moving in the same central Hartree-Dirac-Slater potential of the neutral atom (so-called the “no hole” model). By contrast, we have taken into account the hole in the atomic shell produced after ionization (the
The hole has been considered in the framework of the frozen orbital approximation \cite{4}. This is the only difference between theoretical models used by Scofield and by Trzhaskovskaya et al. Otherwise the atomic models are identical. In particular, both calculations of photoionization cross sections have been performed with allowance made for all multipole orders of the photon field.

As to our calculations, the subshell cross sections are calculated with a numerical accuracy of 0.1%. The accuracy has been verified \cite{8} by comparing our results with benchmark relativistic calculations for one-electron systems by Ichihara and Eichler \cite{9}.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{fig1.png}
\caption{Comparison of photoionization cross sections obtained by Scofield \cite{2} $\sigma(S)$ without regard for the hole in the atomic shell after ionization, with our values calculated without $\sigma(T,nh)$ and with $\sigma(T,h)$ regard for the hole versus atomic number $Z$. The photon energy $k = 1.254$ keV. Solid, $\sigma(T,nh)/\sigma(S)$; dashed, $\sigma(T,h)/\sigma(S)$; dark circles, erroneous values presented by Seah and Gilmore in Fig. 4(a) from \cite{1}.
\end{figure}

In Fig. 1, the proper ratio of cross sections calculated by us and by Scofield \cite{2} $R_\sigma = \sigma(T)/\sigma(S)$ is presented versus the atomic number $Z$ for the $1s$ and $3d_{5/2}$ shells at the photon energy $k = 1.254$ keV. Our calculations have been performed in two different ways: using exactly the same model as Scofield (see \cite{7,10}), that is the “no hole” model (solid lines) and using the “hole” model \cite{4,5,6} (dashed lines). Dark circles refer to the wrong ratio $R_\sigma$ shown by Seah and Gilmore in Fig. 4(a) from \cite{1}. As evident from Fig. 1, solid lines practically coincide with the value $R_\sigma = 1.0$ because as has been shown earlier, our calculations \cite{7,10} using the “no hole” model agree with those by Scofield \cite{2} within $\sim 1\%$. Dashed lines show that taking the hole into account results in a difference $\lesssim 12\%$ in values of $\sigma$ for the cases under consideration. Dark circles located below $R_\sigma = 1.0$ demonstrate that erroneous values of the ratio presented by Seah and Gilmore diverge from correct values just by up to a factor of 5. Dark circles located above $R_\sigma = 1.0$ demonstrate the invalid comparison (see point (ii))
between $\sigma(T)$ and $\sigma(S)$ for the 3$d_{5/2}$ subshell which is the open one for elements with $Z \leq 28$.

We have also checked that cross sections $\sigma$ for all appropriate shells of Ne and Ba for the photon energy $k = 3.0$ keV calculated by us using the “no hole” model agree with results by Scofield [3] also within $\sim 1\%$. A deviation of our values of $\sigma$ obtained by the use of the “hole” model from data [3] does not exceed 8\% rather than 56\% claimed in [1].

Values of photoelectron angular distribution parameters presented in [4, 5] have also been extracted by Seah and Gilmore erroneously (see point (i)). We show in Fig. 2 our correct calculations of parameter $\gamma$ (solid lines) and erroneous values presented in Fig. 1(a) from [1] (dashed lines). The $Z$-dependence of $\gamma$ is given for the photon energy $k=1.254$ keV and for the 2$s$, 2$p_{1/2}$, and 3$p_{1/2}$ shells. As is seen in Fig. 2, for a specific shell, solid and dashed lines coincide for low $Z$ when the binding energy is small as compared with the photon energy. As the binding energy increases and the photoelectron energy decreases, correct and erroneous curves become widely separated. The maximum discrepancy may be much more than 1.45 which is pointed out in [1]. Erroneous value of $\gamma$ may differ from correct $\gamma$ up to many times and even change sign as in the cases of the 2$s$ and 2$p_{1/2}$ shells. It is obvious that the results presented in Figs. 1(b), 4(b), 4(c), 5, 11, and 12 of paper [1] are erroneous for the same reason.

Comparison between our calculations of the non-dipole parameters $\gamma$ and $\delta$ and calculations by Scofield [3] for several subshells of neon, copper, and barium is presented in Table I.

We list ratios $R_{\gamma} = \gamma(T)/\gamma(S)$ and $R_{\delta} = \delta(T)/\delta(S)$ where our calculations (T) have been performed using two models: “no hole” and ”hole”. We omit cases where magnitudes of $\gamma$ and $\delta$ are very close to zero. Photon energy is equal 3.0 keV.
TABLE I: Ratios of the non-dipole photoelectron angular distribution parameters $\gamma$ and $\delta$ calculated by us (T) with and without regard for the hole to those calculated by Scofield (S) without regard for the hole [3]. Photon energy $k$=3.0 keV. $R_{\gamma} = \gamma(T)/\gamma(S)$ and $R_{\delta} = \delta(T)/\delta(S)$.

| Z Shell | no hole $R_{\gamma}$ | no hole $R_{\delta}$ | hole $R_{\gamma}$ | hole $R_{\delta}$ |
|---------|----------------------|----------------------|-------------------|-------------------|
| 10      | 1.00                 | 1.00                 |                  |                  |
| 2s      | 1.00                 | 1.00                 |                  |                  |
| 2p_{1/2} | 1.04 0.94 1.03 0.94  | 1.03 0.96 1.02 0.96  |                  |                  |
| 29      | 0.98                 | 1.44                 |                  |                  |
| 2p_{1/2} | 1.01 0.96 1.01 0.95  | 1.00 0.96 1.01 0.97  |                  |                  |
| 2p_{3/2} | 1.00 0.94 1.00 0.95  | 1.00 0.94 1.00 0.95  |                  |                  |
| 3s      | 0.99                 | 1.02                 |                  |                  |
| 3p_{1/2} | 1.01 0.94 1.00 0.95  | 1.00 0.94 1.00 0.95  |                  |                  |
| 3p_{3/2} | 1.00 0.94 1.00 0.95  | 1.00 0.94 1.00 0.95  |                  |                  |
| 3d_{3/2} | 1.03 0.94 1.03 0.94  | 1.02 0.95 1.02 0.95  |                  |                  |
| 56      | 3s      | 1.03                 | 0.77              |                  |
| 3p_{3/2} | 1.20 0.90 1.98 0.95  | 1.01 0.96 1.02 0.95 |                  |                  |
| 3d_{3/2} | 1.00 0.98 1.00 0.98  | 1.00 0.98 1.00 0.98 |                  |                  |
| 4s      | 1.00                 | 1.02                 |                  |                  |
| 4p_{1/2} | 1.04                 | 1.10                 |                  |                  |
| 4p_{3/2} | 1.05 1.09 1.10 1.09  | 1.00 0.97 1.01 0.97 |                  |                  |
| 4d_{3/2} | 1.00 0.98 1.00 0.98  | 1.00 0.98 1.00 0.98 |                  |                  |
| 5s      | 0.97                 | 0.97                 |                  |                  |
| 5p_{1/2} | 1.05                 | 1.06                 |                  |                  |
| 5p_{3/2} | 1.02 0.94 1.03 0.94  | 1.02 0.94 1.03 0.94  |                  |                  |
Table I demonstrates that there is good agreement between calculations [3] and our results obtained in the same “no hole” model. As is seen, in the majority of cases, the parameters $\gamma$ and $\delta$ are little affected by taking the hole into account. However there exists a considerable deviation of $R_\gamma$ from the value $R_\gamma = 1.0$ for several cases, for example, $R_\gamma = 1.98$ for the $3p_{3/2}$ shell in Ba, $R_\gamma = 1.44$ for the $2s$ shell in Cu, and $R_\gamma = 0.77$ for the $3s$ shell in Ba.

![Diagram](image.png)

**FIG. 3:** The $k$-dependence of the parameter $\gamma$ for the $3p_{3/2}$ shell of the barium atom. Solid, calculations without regard for the hole after ionization; dashed, with regard for the hole.

This difference is associated with the fact that the $k$-dependence of $\gamma$ has a minimum not far from $k=3.0$ keV. So curves $\gamma(k)$ obtained with and without regard for the hole are shifted relative to each other as is seen in Fig. 3 for the $3p_{3/2}$ shell of barium. Nonmonotonous behaviour of the parameters when curves $\beta(k), \gamma(k)$, and $\delta(k)$ may take the form of oscillations has been discussed at length in our paper [11]. In such cases, all assumptions underlying the calculation, a minor difference in binding energies, and other calculational details may have a great impact on values of the parameters.

In summary it should be emphasized that we have clearly demonstrated that dramatic deviations of the results by Trzhaskovskaya *et al.* from those by Scofield and consequently, the deviation of our results from experimental data reported by Seah and Gilmore, do not actually take place and are due to errors (i) and (ii) and shortcomings (iii) in paper [1]. Reasonable deviations between the two calculations are associated with somewhat different atomic models used in [2, 3] and in [4, 5, 6].
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