

PHYS 211A Final Paper

Jennifer Ito

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I. An Introduction

“Atomic Shielding Constants” written by John Clarke Slater in 1930 is a pivotal piece of work in atomic, molecular, and solid-state physics. In this paper, Slater established two main ideas. The first is writing the electron wavefunction approximation for atoms beyond fluorine. The second is generating a set of rules to determine the atomic shielding constants. For this paper, I will be focusing on the latter. After providing an overview of Slater’s paper with regards to the atomic shielding constants, I will explore how his work has been modified, and how his original work continues to be used today. This is merely a sliver of the work that Slater contributed in his lifetime to the realm of physics.

Before beginning, a couple variables will be used multiple times so they will be defined here. Throughout this paper, I will be using the letter Z to refer to the atomic number of an atom. Additionally, I will be using Z_{eff} to refer to the effective nuclear charge which is the nuclear charge on the electron that is modified by the other electrons around it. This modification is captured numerically by the shielding constant. In general, $Z_{eff} = Z - s$ where s is the shielding constant.

II. The Author

John Clarke Slater lived from December 22, 1900 to July 25, 1976. Slater is remembered as an accomplished physicist pioneering theories in atomic, molecular and solid-state physics. He was also a forerunner of education in that he was influential in generating a curriculum at MIT that allowed graduate students to finish their studies in America instead of having to travel to Europe [1]. Additionally, he was an author having written at one point fourteen books in thirty-five years [1]. His career consisted of simultaneously writing books, teaching courses, and supervising student research while still conducting his own [1]. Additionally, Slater established the Solid State and Molecular Theory Group within the MIT physics department [1]. He was a Sheldon Traveling Fellow and Guggenheim Fellow and was awarded the Irving Langmuir Prize in Chemical Physics as well as the National Medal of Science [2]. His faculty and research positions included Harvard, MIT, Cambridge University, University of Leipzig, Brookhaven National Laboratory and University of Florida [2].

Although this paper will focus on the shielding constants Slater developed, it would be remiss to not mention at least some of the other works Slater achieved. As mentioned earlier, Slater expanded the atomic wavefunction approximation which is now known as Slater-type orbitals. He is also the ‘Slater’ from the Bohr-Kramers-Slater theory or BKS theory. Although this theory contradicts Einstein’s claim that light was quantized, Slater actually embraced Einstein’s work when he approached Bohr and Kramers [3]. Slater himself had no hand in writing the paper, but Bohr and Kramers gave him credit for their inspiration in coming up with a theory that countered Einstein’s. Slater also created an expression known as the Slater determinant for antisymmetric wavefunctions. Additionally, Slater did a lot of work during World War II on microwave transmission and wrote a book called as such [1]. He also believed that it was the development of solid-state electronics that instigated the postwar industrial strength of the United States instead of nuclear physics [4].

III. The Paper [5]

In his paper “Atomic Shielding Constants,” Slater generates rules that define atomic shielding constants for simple atomic wave function approximations. He builds upon previous work done by Zener who developed atomic wave functions for atoms from lithium to fluorine. Although Slater does not use the same method as Zener, Slater created his rules to match empirical values of x-ray spectra. At the time, work

by Linus Pauling was the standard for atomic shielding constants, but Slater claims his are simpler and more accurate.

First, Slater argues from Zener and Hartree that the only relevant part of an electron wave function is the radial part of the asymptotic form at large distances of the hydrogen-like wave function. Slater generates an exponential form wave function without any nodes as they were shown to be unimportant by Zener. This wave function is a function of the effective quantum number (n^*), the actual charge on the nucleus (Z), and a screening constant (s). The equation is shown below:

$$r^{n^*-1} e^{-\left(\frac{Z-s}{n^*r}\right)}$$

For each electron, there are rules to assign n^* and Z_{eff} values that Slater devised. Then these single electron wavefunctions can be combined into functions for the whole atom. The rules are as follows:

1. The effective quantum number n^* is given based on the real principal quantum number n .

n	1	2	3	4	5	6
n^*	1	2	3	3.7	4	4.2

2. To find the shielding constant, the electrons are divided into the following groups: 1s; 2s, p; 3s, p; 3d; 4s, p; 4d; 4f; etc. The s and p orbitals are grouped together, but the d and f orbitals are separate. The shells are arranged from the inside out based on the listed order.
3. For each electron group, the shielding constant is formed using the rules below. For a visual aid, see Figure 1.
 - a. For a given electron, nothing from an outer shell is considered
 - b. If there are other electrons in the group, $s = 0.35$ for each other electron except for the 1s group, then $s = 0.30$
 - c. There are two different cases here:
 - i. If the current shell is an s or p shell, then for each electron with one total quantum number less, each electron contributes 0.85. For each electron deeper, each electron contributes 1.00
 - ii. If the current shell is a d or f shell, then each electron with a smaller total quantum number contributes 1.00

To help solidify the rules, one of Slater's examples is provided using Fe with $Z = 26$.

Electron Group	Number of electrons
1s	2
2s, p	8
3s, p	8
3d	6
4s	2

Table 1: Electron list for iron (Fe) atom

For an electron in each of the listed group, Z_{eff} is calculated as follows:

Electron Group	Total shielding constant s	Effective nuclear charge Z_{eff}
1s	1×0.3	$26 - 0.3 = 25.7$
2s, p	$7 \times 0.35 + 2 \times 0.85 = 4.15$	$26 - 4.15 = 21.85$
3s, p	$7 \times 0.35 + 8 \times 0.85 + 2 \times 1.0 = 11.25$	$26 - 11.25 = 14.75$
3d	$5 \times 0.35 + 18 \times 1.0 = 19.75$	$26 - 19.75 = 6.25$
4s	$1 \times 0.35 + 14 \times 0.85 + 10 \times 1.0 = 22.25$	$26 - 22.25 = 3.75$

Table 2: Examples of calculating shielding constants and effective nuclear charge for a given electron in the electron group.

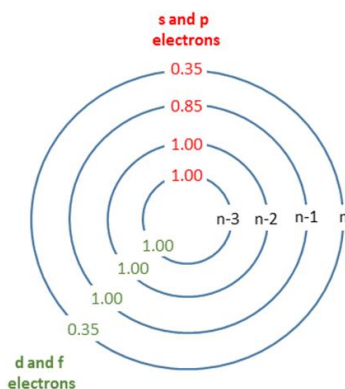


Figure 1: A visual representation of Slater's Rules given an atom of arbitrary n . For an electron with principle quantum number n , the shielding constant for every other electron is given based on its own principle quantum number and orbital. [6]

Next, Slater goes on to show that his rules for the shielding constant give total atomic energy values that are reasonable. He quotes from Zener and further supports that the total energy required to remove all electrons from the nucleus to an infinite distance is the sum of $((Z - s)/n^*)^2$ for all the electrons in the atom or ion. He goes on to give examples of carbon and iron and some alkalis as well. Slater argues that the energies obtained are accurate, but he also cautions that they are not to be scrutinized. Additionally, the main criteria for setting his atomic shielding rules is so that these energy values are consistent with experimental results.

Another usefulness of the shielding constants is calculating the sizes of atoms and ions. By differentiation, Slater claims that the radial charge density of an electron shell is $(n^*)^2/(Z - s)$. This can be used to calculate atomic radii for neutral atoms. It can also be used for internuclear distances. Assuming that for binding, the electrons forming the bond would want to be maximally overlapping, it is reasonable that the internuclear distance is the sum of the radii. Therefore, using these radii, one could approximate internuclear distances in valence compounds and metals for substances that exist in the atomic state. He lists multiple tables that demonstrate the ratio between the internuclear distance observed to the sum of the calculated atomic radii. For valence electrons in the p orbitals, the ratio is roughly one. For valence electrons in the s orbitals, the ratio is roughly two-thirds. Either way, Slater asserts that this is a good way to roughly predict the size of the internuclear distances.

As mentioned earlier, Slater provides multiple tables to show that the summing of radii is a good approximation for calculating the maximum radial density in charge distribution of atoms and the

internuclear distances in molecules and crystal structures. A few examples of molecular and crystal internuclear distances are listed below. Slater is aware that substances with one or both valence p electrons, the ratio is consistently around one; however, for substances with both valence s electrons, the ratio is roughly 0.7.

Substance	Valence	Distance Observed	Sum of Radii	Ratio of Obs/Calc
H ₂ O molecule	p-electrons	1.07	1.00	1.07
H ₂ molecule	s-electrons	0.76	1.06	0.71
Pb crystal	p-electrons	3.48	3.32	1.05
K crystal	s-electrons	4.50	6.64	0.68

Table 3: A listing of molecule and crystal internuclear distances comparing the observed with Slater's results

Ionic radii are another characteristic that Slater uses his radial charge density calculation for and therefore, his atomic shielding constants. He claims that the appropriate ionic radius is when the radial density roughly becomes ten percent of its maximum value. Numerically solving the problem led Slater to discover that the radius is a constant multiplied by the maximal radial density for each effective quantum number n^* . From this, he claims that the observed and calculated values are in good agreement and gives a table with some examples. He also maintains that this confirms that these ionic compounds are made of atoms that exist as ions.

Ion	Observed radius [\AA]	Calculated radius [\AA]
O ⁻	1.32	1.37
S ⁻	1.69	2.16
Rb ⁺	1.50	1.58

Table 4: Examples of calculating ionic radii

Finally, Slater very briefly states that ones can check his calculated size of atoms by using diamagnetic susceptibility. Using his wavefunction, he derives an expression that is dependent on the effective quantum number n^* and Z_{eff} . He lists a very short table of three inert gases that he calculated. However, he does not do any other analysis as to whether or not he believes these are in agreement.

$$\frac{(n^*)^2(n^* + \frac{1}{2})(n^* + 1)}{(Z - s)^2}$$

Inert gas	Calculated	Observed
He	2.07	2.34
Ne	7.08	8.31
A	23.37	22.6

Table 5: Examples of sizes of atoms comparing the observed value to that calculated using diamagnetic susceptibility

IV. Further Work

Slater actually modified his own work in 1960. One of the many books he wrote is *Quantum Theory of Atomic Structure* [7]. In the first volume of this series, Slater presents a modified expression for the effective charge seen by a given electron. He keeps the term for electrons that are closer to the nucleus (inner shielding) but adds a term for the electrons that are further away (outer shielding) than the electron being considered. The total Z_{eff} is then the actual nuclear charge minus the inner and outer shielding terms.

The difference in having the outer shielding term or not depends on if one is looking at the effective nuclear charge for calculating energy or for the wave function. Slater shows in his book that the outer shielding term seems to account for the discrepancy between effective nuclear charges for the energy and wave function. He also gives a relationship between the two which is as follows:

$$Z_{energy} - r \frac{dZ_{energy}}{dr} = Z_{wave}$$

Three years after Slater's book was published, an Italian chemist Enrico Clementi produced a paper with values for atomic screening constants that were calculated while considering both the inner and outer shielding electrons [8]. With Slater-type orbitals and the self-consistent-field (SCF) method by Hartree, Clementi calculates a parameter called the orbital exponent ξ defined by the equation below. The numerator is the effective nuclear charge Z_{eff} felt by a given electron and n is a function of the principle quantum number. In this notation, σ is the shielding constant.

$$\xi = \frac{(Z - \sigma)}{n}$$

Clementi uses a program developed by C. C. L. Roothaan to optimize ξ . An interesting bit of history is that this program was created for an IBM 7090 computer which was first introduced in 1959. After analyzing the results, Clementi proposed a modified set of Slater's rules that can be found in his paper but will not be written out here due to length and complexity. Clementi points out that Slater assumes that the shielding constant is independent of certain quantum numbers and spin multiplicity. Slater's original shielding constant is simply a function of the principle quantum number and the number of electrons that contribute to the inner shielding. Clementi modifies the shielding constant to be a function of the principle quantum number, the total number of electrons, the angular orbital quantum number, the total angular momentum, and spin multiplicity. Clementi shows this modified set of rules is verified by the analysis done in the paper. In 1967, Clementi extends his analysis to atoms with 37 to 86 electrons [9]. This update to Slater's rules has been widely referenced as shown through the 2,528 citations this paper has received. It rivals the 2,597 citations Slater's original paper received according to Web of Science.

One year later, Gerald Burns in Switzerland published a paper titled "Atomic Shielding Parameters" where he focuses on the wave function expression instead of minimizing the energy [10]. He takes Slater's wave function and a hydrogenic wave function and compares the expectation values of each of these to that of a Hartree-Fock wave function expectation value. There were more than 90 wave functions studied including those up to Z of 70. From this, Burns generated a new set of rules for finding the shielding constant.

A key point he makes is that the method used for finding the atomic shielding constants are dependent on if one is minimizing energy values or strictly looking at just the wave functions which echoes Slater in his book. Burns also wrote footnote about discussing Clementi's work and compares their values. Burns mentions that Clementi's effective Z for up to $Z=36$ are roughly in agreement though consistently higher than what Burns calculates using his own method. This implies that Burns' shielding constants are higher than Clementi's.

Sakai and Anno in Japan published a paper in 1974 prescribing a new set of rules for calculating Slater-type shielding constants and effective principle quantum numbers [11]. In this paper, the authors work to match Slater-type atomic orbitals to Hartree-Fock atomic orbitals only for atoms with 1s, 2s, and 2p electrons. In doing so, they come up with an expression for calculating energy and Z_{eff} . The effective Z is a function of the shielding constants, and the energy is a function of the effective nuclear charge. Since

the energy values can be determined experimentally, one can find the effective nuclear charge which means one can deduce the shielding constants.

Through this process, Sakai and Anno calculate shielding constants and compare their values to Slater's and Clementi's work. Depending on which electron is acting on which, their values can vary by as much as half of what Slater and Clementi produced. It is implied that the values by Slater and Clementi are just listed as reference since the discrepancies are not actually analyzed. It would seem that the different values are due to the atomic orbital wave function basis and energy fitting used.

In 1981, Bessis and Bessis published a paper named "Analytic atomic shielding parameters" in France [12]. They summarize the work of Slater, Roothaan, Clementi, and Burns pointing out that all these use numerical fittings. In this paper, they present a method for calculating the shielding constants using what they call "simple mathematics" and without a fitting analysis. They begin with the Schrodinger equation and look at only the radial screening. Then, they classically write the electron-electron interaction term and Taylor series expand limiting themselves to the first order in $1/r$. In the end, they get an expression for the shielding constant as the following. The indices i and j are for denoting electrons.

$$\sigma_i = \sum_{j \neq i} \left\{ 1 + \left[\frac{3n_j^2 - l_j(l_j + 1)}{3n_i^2 - l_i(l_i + 1)} \right]^2 \right\}^{-3/2}$$

This equation includes the dependence on l but if $l = 0$, then the summation reduces to

$$\sigma_i = \sum_{j \neq i} \left\{ 1 + \left[\frac{n_j}{n_i} \right]^4 \right\}^{-3/2}$$

A table is provided in their paper comparing their work to Slater, Clementi and Burns. They calculate the orbital exponent ζ which is the same equation as shown earlier. They conclude that their values are adequate mentioning that their values are equivalent to the trends found by Clementi.

In a more recent publication, it is bluntly stated the limitations of Slater's rules [13]. In their abstract, they state, "Our work shows that Slater's rules are not appropriate for predicting trends or screening [shielding] constants." The authors' discussion counters the notion that the rules Slater created are accurate for most atoms. They state that Slater's rules are good for electrons in orbitals that have a total quantum number less than four. Additionally, they argue that Slater's method cannot describe ionization energies across the periodic table.

It is interesting to note that Slater developed his rule set in order to match the then current x-ray spectra and not as a rigorous method for determining shielding constants. As shown through the various scientists that followed Slater, this rule set was modified conceptually to more accurately determine shielding constants in more complex electron configurations. Yet, Slater's rule set has seem to be accepted on the whole as a good approximation across the periodic table which is not something Slater seems to claim in his original paper. If he were still alive today, it would be intriguing to know Slater's response to the evolution of his rule set.

V. Using Slater's Rules

In filtering through the two and half thousand citations Slater's paper has on Web of Science, there are many more references to Slater-type orbitals than directly to Slater's rules for calculating the shielding constant. However, it could be argued that in using the Slater-type orbitals, one would need the shielding

constants to find Z_{eff} . In spite of this, there were some recent papers found that referenced Slater's rules for shielding constants which are listed in the following paragraphs. Through these examples, the importance of having atomic shielding constants is also shown.

A paper in 1971 by Lawrence Snyder expands Slater's expression for the energy of an atom to find the energy of core-ionized atom [14]. Snyder explains from Koopmans' theorem that the assumption that atomic or molecular orbitals remain unchanged when ionized also implies that the shielding constants for remain constant as well. Therefore, these shielding constants would be used in calculating the energy of the core-ionized ion. However, this does not minimize the energy so Snyder uses Slater's atomic shielding constants to generate a more general energy expression that is then used to study Koopmans' theory on the ionization potential for core electrons.

In 2015, Lamour et. al, wrote a paper on calculating the charge-state distributions for ion-solid collisions [15]. Exploring the charge-state distributions of projectile ions through solid targets is important for material science and designing and analyzing atomic and nuclear physics experiments. The authors use Slater's rules to account for calculating the effective nuclear charge to be used in calculating radiative and Auger decay rates that are necessary for their algorithm ETACHA to calculate the charge-state distributions.

Another paper published in 2015 studies the photochromic effect on divalent rare earth ions [16]. In order to approximate the lattice distortion of the divalent rare earth ions, this study used the conventional dependence on the ionic radius. The authors use Slater's work on shielding constants as a resource to approximate the ionic radii.

A current example and application of Slater's rules and atomic shielding constants in general is the estimation of the electron-phonon coupling constant done by Kaneko et al [17]. In their paper, they use another piece of work of Slater's. To find the coupling constants, they use the Slater-Koster parameters and Slater-type orbitals. In doing so, they need the orbital exponent ξ which requires using shielding constants. Since Clementi's modifications generated a value such that the overlap integral could be solved analytically, they decided to use Clementi's adjusted set of Slater's rules. Still, the authors credit Slater's original work and shows an application of shielding constants in solids.

VI. Conclusion

Over the last 90 years, Slater's rules have remained as a foundation for approximating the atomic shielding constant in order to calculate Z_{eff} , to use simpler atomic wave functions and to calculate atomic energy. Slater also contributed an astounding amount of knowledge to the physics community through his various other work in atomic, molecular and solid state studies in addition to his work with electromagnetic radiation amongst other things. His passion to create a better academic environment for his students is also inspiring.

As far as his rules for finding the atomic shielding constants, they have been given the proper name of Slater's Rules and are still being included in curriculum. His work provided a simple approximation for finding shielding constants for multiple applications from crystal internuclear spacing to atomic radii to orbital exponents. Because of their simplicity and order-of-magnitude approximations, they are ideal for educational purposes [18]. Over time other scientists modified Slater's Rules or generated a new method for calculating shielding constants that continued to refine the process that Slater is known for.

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$$\sigma = \sum_i \left[\left\{ \frac{1 + \left(\frac{3m_i^2 - l_i(l_i+1)}{3m_j^2 - l_j(l_j+1)} \right)^4}{\left(\frac{3m_j^2 - l_j(l_j+1)}{3m_k^2 - l_k(l_k+1)} \right)^4} \right\}^{-\frac{3}{2}} \right]$$

$$- \sum_{\substack{i \neq j \\ j \neq k}} \left[\left\{ \frac{1 + \left(\frac{3m_j^2 - l_j(l_j+1)}{3m_k^2 - l_k(l_k+1)} \right)^4}{\left(\frac{3m_k^2 - l_k(l_k+1)}{3m_h^2 - l_h(l_h+1)} \right)^4} \right\}^{-\frac{3}{2}} \right]$$

$$+ \sum_{j \neq h} \left[\left\{ \frac{1 + \left(\frac{3m_j^2 - l_j(l_j+1)}{3m_h^2 - l_h(l_h+1)} \right)^4}{\left(\frac{3m_h^2 - l_h(l_h+1)}{3m_i^2 - l_i(l_i+1)} \right)^4} \right\}^{-\frac{3}{2}} \right]$$

i- all inner electron including those of same shell

j-electron whose z_{eff} is to be measured

k- all outer electrons not including those in same shell

h- all inner electron including those of same shell

we will add and subtract such notations for multi electron atom to find screening constant. Understand the pattern and form the terms for multi electron atoms.