COMPUTATIONAL ANALYSIS OF THE RELATIVE DECAY CONSTANTS FOR ^{7}BE, ^{7}BE^{+}, AND ^{7}BE^{++}

by

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ABSTRACT

COMPUTATIONAL ANALYSIS OF THE RELATIVE DECAY CONSTANTS FOR ^{7}BE, ^{7}BE$^+$, AND ^{7}BE^{++}

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The actual decay constant for neutral beryllium 7 (^{7}Be) is unknown because it has always been measured with a substantial loss of its 2s electrons due to bonding or interstitial effects. By considering free ^{7}Be ions (such as may appear in a low density non-neutral plasma) we can potentially calculate the electron charge density at the nucleus with more accuracy and this can be used to calculate relative changes in the decay constant for ionized states of ^{7}Be. We use both Hartree–Fock self-consistent field (HF SCF) and Density Functional Theory (DFT) methods for calculating the relative changes in the decay constants for ^{7}Be, ^{7}Be$^+$, and ^{7}Be^{++} and find that there is a non-linear relationship between the decay constant and the fractional amount of 2s electrons still present in the nucleus.

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I. INTRODUCTION

For many years, elements that only decay through electron capture have been known to be susceptible to changes in their half-life [1,2]. These changes have been achieved by subjecting the particular element to an external environment that essentially changes the electron charge density near the nucleus and thus the probability of an electron being captured. Since the only atomic orbitals that give finite electron densities at the nucleus are s orbitals, the shape of the s orbitals has the greatest effect on the electron capture rate [3]. An element's s orbitals can be manipulated by changing its physical [4] or chemical state [2,5,6], by exposing it to extreme pressures [6–10] or temperatures [11,12], or by ionizing its atoms [13]. Although any element with this property should exhibit these characteristics, it has been much harder to observe in heavier elements because the valence electrons (those most susceptible to outside influences) are so far away from the nucleus, or the shielding is so great, that they exhibit a very small effect [3,14,15]. Thus only for lighter elements will the wave functions of the valence electrons noticeably overlap with that of the nucleus. The lightest element that decays solely by electron capture is beryllium 7 (^{7}Be) and thus it is a prime candidate for understanding more fully the physics of electron capture.

Despite the long history of research done on ^{7}Be, there is still no known half-life for neutral ^{7}Be. Almost all of the half-life measurements to date are of ^{7}Be embedded interstitially in other elements; however, because this affects the electron density near the nucleus, none of these measurements truly represent the half-life of ^{7}Be [16]. The "accepted" half-life is merely an average of all of these measurements and has no more correlation with the actual half-life of neutral ^{7}Be than any one measurement on its own, i.e., taking an average was not done with the express purpose of obtaining a more accurate half-life.

One of the most important places where the half-life of ^{7}Be is used is in the Standard Solar Model (SSM) to calculate the boron 8 (^{8}B) solar neutrino, one of the primary neutrinos that we can detect [17]. ^{7}Be is created in the proton-proton cycle of the sun and is a necessary precursor to ^{8}B. However, the decay rate for ^{7}Be used in the calculation came from terrestrial measurements assuming that all of its 2s electrons were still present [18]. Because every host material used in experiments thus far has had a different electron affinity than that of ^{7}Be, these experiments measured the half-life of ^{7}Be with a substantial fraction of 2s electrons missing. While this is only one among many sources of errors in the SSM, after the measurement of the ^{8}B neutrino flux to within 5% uncertainty by the Sudbery Neutrino Observatory [19], there has been a push to increase the accuracy of the SSM (still at about 20% uncertainty) in order to compare theory and experiment [20].

Another place ^{7}Be is created is in the upper atmosphere of the Earth; it is a natural byproduct of spallation of cosmic rays colliding with oxygen and nitrogen. When the Long-Duration Exposure Facility (LDEF) was retrieved and analyzed after orbiting Earth for six years in low orbit, there was an unusually high concentration of ^{7}Be found [21,22]. Because of the dynamic process in which ^{7}Be is formed in the atmosphere, it is likely that it forms in an ionized state. A longer half-life for ^{7}Be^{+} caused by having fewer electrons near the nucleus could possibly explain the unexpected amount of ^{7}Be on the LDEF. Thus it is not only important to find the decay rate for neutral ^{7}Be, but also for ^{7}Be$^+$. Furthermore, a full investigation into the relationship between decay rate and 2s electrons near the nucleus would be quite revealing. Recently Das and Ray predicted that this relationship was linear (Fig. 1) [23]. However, the data used had a fairly tight spread

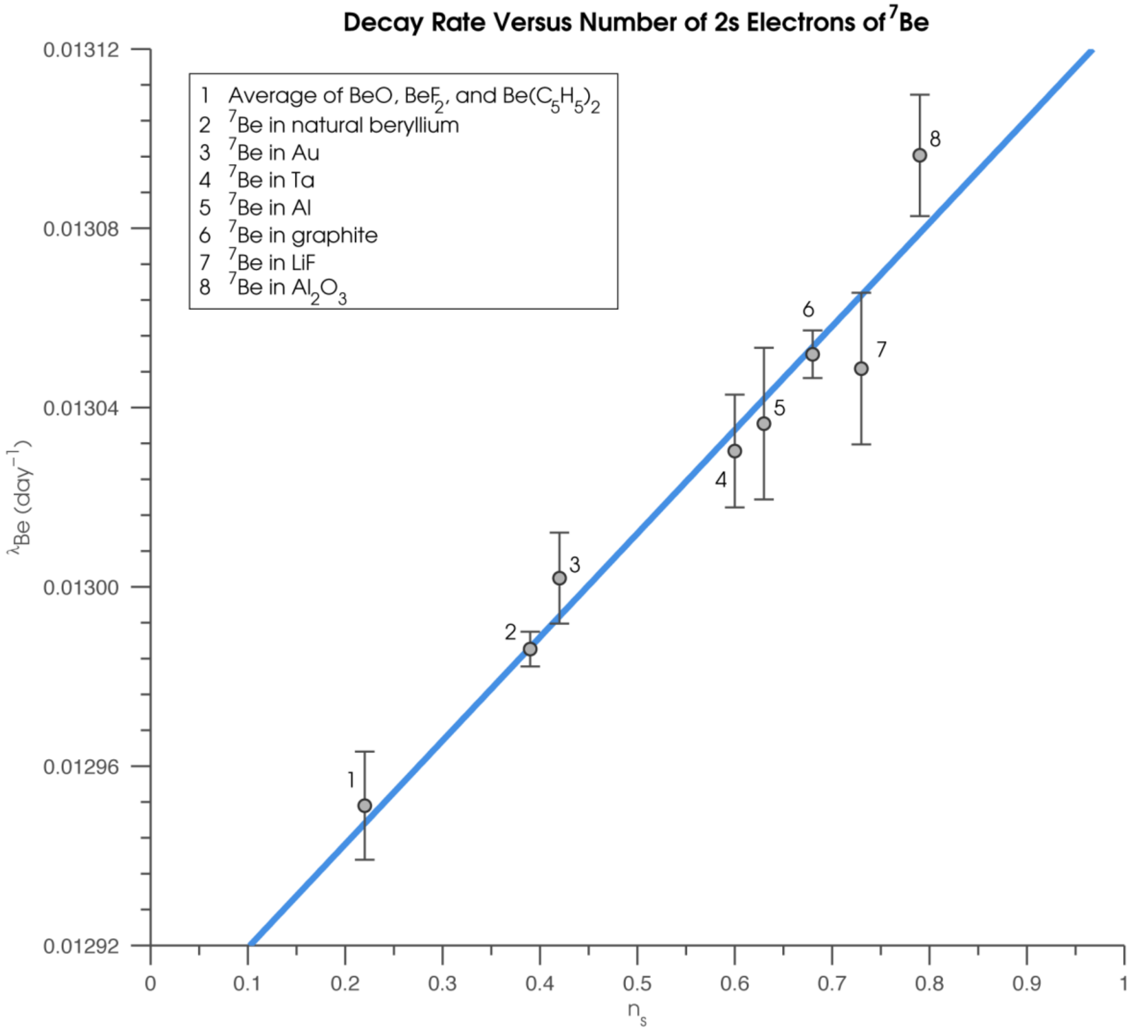


Fig. 1 This is a graph taken from Das and Ray's paper [23] that shows the proposed linear relationship between the decay constant and the fractional amount of 2s electrons (n_s) still present in the nucleus. The numbered points were calculated by Das and Ray using a tight-binding linear muffin-tin orbital method on ^{7}Be atoms in the media listed in the graph.

(~3/10 of the proposed range) and may or may not represent the true relationship over the entire range of 2s electrons near the nucleus. In addition to the two previously mentioned decay rates, it would be necessary to compute a third decay rate for ^{7}Be^{++} as well. Therefore, a correct calculation and/or measurement of the half-lives for ^{7}Be, ^{7}Be$^+$, and ^{7}Be^{++} would be advantageous for many different reasons.

The plasma research group at Brigham Young University is the first to try to measure the half-life of ^{7}Be when it is free from other materials [24]. They will do this by creating a very low density, non-neutral plasma of singly ionized ^{7}Be. A low density plasma minimizes the interaction between atoms while a non-neutral plasma ensures that there are no free electrons to affect the half-life measurement. One advantage to this experiment is the corresponding theoretical calculation is less complicated since it only needs to take into account a single atom. Additionally, the amount of 2s electrons still present in the atom is known exactly without recourse to other calculations. Therefore this single atom calculation could potentially produce results more reliable than others, and will hopefully provide experimental data to substantiate the theory. Using this as a model, we will be looking at the electron densities of ^{7}Be, ^{7}Be$^+$, and ^{7}Be^{++} and their corresponding decay rates.

II. THEORY

Although Bambynek *et al.* did a fairly comprehensive study of different calculation methods for β^-, β^+, and electron capture decay rates [25], both the derivations and the calculations are rather lengthy and are not as easily adapted to compare changes in the decay rate ($\Delta\lambda$) due to ionization as the method presented by Bukowinski [9]. The latter is much more transparent and results in a simple relation for $\Delta\lambda_{EC}$ that only depends on the electron charge density at the nucleus of both neutral and ionized atoms (ρ and ρ' respectively) and the neutral decay constant (λ_0). The following is a reproduction of the derivation of $\Delta\lambda_{EC}$ given by Bukowinski.

^{7}Be decays 100% of the time by electron capture into ^{7}Li (89.56% directly into the ground state of ^{7}Li and 10.44% into an excited state of ^{7}Li followed almost immediately by γ decay into its ground state). The electron capture process, regardless of the two branches, follows the reaction

$$^{7}\mathrm{Be} + \mathrm{e}^{-} \rightarrow {}^{7}\mathrm{Li} + \nu_{\mathrm{e}} \ , \tag{1}$$

where e^- is an electron (usually from the 1s orbital, but not necessarily) and ν_e is a neutrino. The probability of this reaction is proportional to the square of the matrix element of the interaction Hamiltonian, H_{int}, between the initial and final states of the atom. Under the Born-Oppenheimer approximation, we may decouple the nuclear and electronic wave functions and, to a good approximation, we may treat the process as a two-body interaction

$$\mathrm{p} + \mathrm{e}^{-} \rightarrow \mathrm{n} + \nu_{\mathrm{e}} \ , \tag{2}$$

where p is a proton and n is a neutron. It then follows that the decay constant for electron capture, λ_{EC}, is given by

$$\lambda_{EC} = \mathrm{c} \cdot \left| \int \psi_n^* \ \psi_\nu^* \ H_{\mathrm{int}} \ \psi_p \ \psi_e \ d\tau \right|^2 \ , \tag{3}$$

where ψ_n, ψ_ν, ψ_p, and ψ_e are the wave functions of the neutron, neutrino, proton, and electron, respectively, and c is a constant of proportionality. Because of the small size of the nucleus, we may approximate equation (3) by

$$\lambda_{EC} = \mathrm{c} \cdot \left|\psi_e(0)\right|^2 \cdot \left| \int \psi_n^* \ \psi_\nu^* \ H_{\mathrm{int}} \ \psi_p \ d\tau \right|^2 . \tag{4}$$

If more than one electron state has non-vanishing amplitude at the origin, the decay constant is the sum of all the individual contributions:

$$\lambda_{EC} = \mathrm{c} \cdot \rho \cdot \left| \int \psi_n^* \ \psi_\nu^* \ H_{\mathrm{int}} \ \psi_p \ d\tau \right|^2 , \tag{5}$$

where

$$\rho = \sum_i \left|\psi_e^i(0)\right|^2 . \tag{6}$$

Making the reasonable assumption that the various nuclear wave functions are not affected by a few megabars of pressure, $\Delta\lambda_{EC}$ may be written as

$$\Delta\lambda_{EC} = \mathrm{c} \cdot (\rho' - \rho) \cdot \left| \int \psi_n^* \ \psi_\nu^* \ H_{\mathrm{int}} \ \psi_p \ d\tau \right|^2 \tag{7}$$

or

$$\Delta\lambda_{EC} = \left(\frac{\rho'}{\rho} - 1 \right) \cdot \lambda_0 = \alpha \cdot \lambda_0 . \tag{8}$$

where ρ' is the total electron density at the nucleus at pressure P, ρ at atmospheric pressure, and λ_0 is the atmospheric pressure decay constant for neutral ^{7}Be. Although equation (8) was derived under the assumption that pressure was the only thing that was changing, the equation is more general. Both Tossel [6] and Lee *et al.* [3] use the same equation assuming that chemical combinations also do not affect the nuclear wave functions. Because this has the same affect ionization has on an atom, we will be able to use this equation as well.

The disadvantage of using this calculation is that it does not provide any decay rates for the ionized atoms. In fact, λ_0 must be known first in order to even find $\Delta\lambda_{EC}$.

However, provided λ_0 were to be obtained, either from the aforementioned methods set forth by Bambynek, *et al.*, or otherwise, both of these obstacles would then be irrelevant. In any case, even without λ_0, valuable insight can be gained from an analysis of just the proportionality factor α, especially since Das and Ray also only consider relative decay rates (the slope of λ vs. average number of 2s electrons, n_s) and admit that their calculations would likely have a vertical offset even though the slope would remain unchanged [23]. Thus, in order to verify the linear relationship between λ and n_s obtained by Das and Ray, we need only see if α produces the same slope over the entire range of n_s or if the relationship is more complex and only appears linear over smaller intervals.

III. METHODS

In order to use equation (8), we need to have some method of calculating electron charge densities at the nucleus. For many-electron atoms, this requires a quantum chemistry program that can numerically solve for the charge density by using a basis set, or trial wave function, that is optimized to give the lowest upper bound on the energy. Most quantum chemistry packages only recognize basis sets that use Gaussian-type orbitals (GTOs, a four-indexed function containing an exponential in r^2) to approximate the atomic orbitals of the electrons, although there are a few programs that are now able to implement Slater-type orbitals (STOs, a four-indexed function containing an exponential only in r).

STOs provide a better representation of the actual atomic orbitals because the exponential allows the existence of a cusp at the nucleus. Unfortunately, there is no analytic solution to its four-indexed integrals and therefore it must be solved numerically. These numerical calculations are computationally very taxing and few programs have tried implementing them. On the other hand, the four-indexed integrals for GTOs do have an analytic solution making calculation times more practical. However, GTOs have drawbacks in other areas; they are rounded instead of cusped at the nucleus and they fall off too quickly at larger radii because of the r^2 dependence. The former is a serious disadvantage to our calculation because we need an accurate electron charge density exactly at the nucleus.

One very basic way to increase the accuracy is to increase the number of functionals used in the basis set. In general, according to Hartree–Fock (HF) theory and the quantum mechanical Variational Principle, increasing the number of functionals will converge on the HF limit giving a more accurate charge density [26]. While this provides a good starting point, HF theory has some inherent drawbacks as well. HF theory uses the fundamental assumption that each electron sees all of the others as a static electric field and ignores the problem of correlation altogether. For this reason, HF theory is used to optimize the functions describing occupied orbitals while functions for correlation between electrons are optimized using theories such as Møller–Plesset (MPn, where n refers to the order of the perturbation), configuration interaction (CI), or coupled-cluster (CC).

Each of these more robust methods has their place and it is important to understand their strengths and limitations when deciding which method is best for a given calculation. MPn theory is a many body perturbation theory and works very well for small perturbations, but its performance decreases as the perturbation increases and, furthermore, the theory does not necessarily converge at higher orders [27]. Thus MPn theory only allows for a partial description of the correlation between electrons. Meanwhile a full CI calculation (using an infinite basis set) does converge and yields an "exact" solution to the non-relativistic, Born–Oppenheimer, time-independent Schrödinger equation; however, some formulations are not size-consistent [28]. Size-consistency is important because it ensures that the quality of the results does not depend on the size of the system, i.e., how many nuclei, how many electrons are in the system, or how far apart or close together they are.

CC theory is a mathematically elegant CI method developed to fix the size-consistency problems that plague many of the CI calculations. Therefore the CC approach would likely be the best approach to calculating an accurate electron charge density. CC theory is a perturbation theory that uses an excited configuration that is "coupled" to the reference configuration and the order of the calculation is determined by the number of excitations allowed in the definition of the excitation operator. Currently in the literature and in computational programs CC theory has only been implemented up to fourth order. The orders are usually denoted by appending CC with the letters S, D, T, and Q that respectively stand for single, double, triple, and quadruple excitations. A four-electron atom would have full description using CCSDTQ, but it is likely that the triples and quadruples would only make very fine corrections to that of the singles and doubles (although doubles by far gives the most significant contribution, singles are needed to account for orbital relaxation and are easily incorporated when already doing doubles) [29]. Therefore, calculations at the CCSD level of theory would most likely be accurate enough for our purposes and it will allow for a full description for at least one of our calculations, $^7Be^{++}$.

All of these methods are dependent on basis sets and even the best theory will produce erroneous results if given a basis set that is too small or badly optimized. In fact, the basis set is often more important that the actual computer package used. This has given rise to hundreds of basis sets and it is often hard to choose which is best for a given calculation. In our case, because we are looking for the electron charge density at the nucleus, the calculation is most strongly dependent on large exponent (tight) functions in the basis set, usually found in the s orbitals. Although tight functions affect chemical bonding very little, they provide a much better description of the electron density curve near the nucleus than diffuse functions [30]. Because our calculations do not involve bonding and depend on the charge density at the nucleus, tight functions are essential for getting accurate results.

S orbitals are also important because they are the only finite orbitals at the nucleus and are the orbitals that contribute the most to the charge density at r=0. Furthermore, in its ground state, ^7Be only occupies the 1s and 2s orbitals adding more importance to the s orbitals. That is not to say that we are only interested in basis sets with strictly s orbitals; Bunge and Equivel show that including angular functions (P, D, F, etc.) slightly improves charge density calculations [31]. Unfortunately, they also found that it was not intuitive as to what combination of them would yield the best charge density. Rather it would require a manual optimization of the charge density for known quantities. Helium (He) would be an ideal candidate for such optimization because of the immense amount of research done on He to very high precision. Consequently, the ideal basis set for our calculation would have a large number of radial functions (20+ s functions) supplemented by a few angular functions as well.

Most basis sets "out of the box" are contracted in some way (i.e. at least one of the basis functions is represented by a linear combination of Gaussians) and almost without exception include a contraction of the s orbitals. Not only does this reduce the number of s orbitals, but it also tends to make the basis more diffuse. Thus, as a general rule, a basis set loses some of its flexibility when it is contracted, especially at the nucleus [32]. Consequently, for any calculation near the nucleus it is almost always wise to uncontract the basis set first. Additionally, most basis sets are designed only for valence electron correlation, but because correlation between both the 1s and 2s electrons is important we will need a basis set that allows for core-valence correlation, e.g., the correlation consistent polarized core-valence n-tuple zeta (cc-pCVnZ) basis set or the weighted core-valence n-tuple zeta (cc-pwCVnZ) basis set. This also means that the frozen core approximation would yield poor results and should not be used for this type of calculation, especially for $^{7}Be^{+}$ or $^{7}Be^{++}$ (the latter would then have no electrons to even correlate). Because basis sets with tight functions are important for properties more sensitive to intrashell correlation, cc-pCVnZ (or similar basis set) would likely be a better candidate than cc-pwCVnZ [33]. However, most basis sets do not have enough s orbital functions and need to be augmented with another basis set, preferably composed exclusively of a large number of s orbital functions. In fact, probably the best option available would be to manually create a new basis set with all of these features and then optimize the exponentials simultaneously until the HF energy is minimized. Fortunately, the calculations are similar enough to one another that we should be able to use the same basis set for all three charge density calculations for ^{7}Be, ^{7}Be^{+}, and ^{7}Be^{++}.

IV. CALCULATION

We will be using NWChem [34, 35] for our initial calculations because of its built-in charge density algorithm (dplot) and because the most recently published basis sets are available in NWChem format from the Environmental Molecular Sciences Laboratory Basis Set Exchange (EMSL BSE) website hosted by Pacific Northwest Laboratory [36–38]. We will be comparing our calculations with previously published charge densities and the calculated hydrogenic charge density for ^{7}Be^{+++} in order to see which basis set yields the best results. Once a suitable basis set is found, we will then use this to calculate all needed charge densities and use them in equation (8) to find relative changes in the decay constant. We will then normalize our data to overlap the data obtained by Das and Ray in order to verify whether there is a linear relationship between the decay constant and the fractional amount of 2s electrons in the atom. Because we are only looking at the 2s shell, we will only be plotting our first three calculations (^{7}Be, ^{7}Be^{+}, and ^{7}Be^{++}). Although the calculation for ^{7}Be^{+++} will be useful in determining our method accuracy, it only has one 1s electron and the charge density at the nucleus behaves much differently than when 2s electrons are present.

NWChem's "dplot" calculation has two available methods. In this paper we will be using both methods and will compare the results obtained from each to see how well they agree. The first approach is the Hartree-Fock self-consistent field (SCF) method. This is an iterative process designed to converge on a set of orbital wave functions that can be used to generate important chemical properties. Initially a guess is made for the wave functions of the occupied atomic/molecular orbitals and from these the one-electron Hamiltonians or Fock operators are constructed. Then by solving the one-electron Schrödinger equation a new set of wave functions are generated and the process repeats. When the convergence criterion is reached, usually when the energy changes by less than a specified amount, the loop is broken and the now "converged" wave functions can be used to generate any physical observable. The major caveat is that SCF calculations are done at the HF level and thus uses the assumption that each electron sees all the others as a static field. Therefore this is only reliable as a preliminary calculation and as a stepping-stone for more accurate theories.

The second method used by "dplot" is density functional theory (DFT). DFT and molecular orbital theory (MO theory) are two very different approaches to the same problem. Whereas MO theory optimizes the wave function, DFT instead optimizes the charge density. Although using a physical observable is not as versatile as the wave function, there are some advantages to taking this approach over MO calculations. First, DFT calculations are guaranteed to never scale worse than N^3, where N is the number of functions used to represent the Kohn-Sham orbitals, and often do much better. Since HF MO calculations usually scale as N^4, DFT calculations are the most cost-efficient method within a certain accuracy [39]. Another important advantage is that DFT calculations do not necessarily need to be fed contracted Gaussians and, under certain representations of the density, even STOs are available [40]. One significant improvement on HF theory is the fact that DFT replaces the HF exchange terms for a more general term that can include information about both exchange energy and electron correlation. Even though DFT does not account for correlation completely, this will potentially give us more accurate results than the SCF method. Hence a DFT calculation with its alternate approach will serve as an important verification of any results obtained by the above SCF method.

We stress that these are initial calculations and that a subsequent calculation using the CCSD theory described above (preferably in a program supporting STOs, e.g., Molpro) will need to be conducted in order to verify the results in this paper.

V. RESULTS/DISCUSSION

We first calculated the electron density at the nucleus for ^{7}Be^{+++} by solving the Schrödinger equation for a hydrogen-like atom with a modified potential for a beryllium nucleus. Even without taking into account fine-structure effects due to spin or relativity, the hydrogenic solution should be accurate to 1 part in 10^4 for Be; this is more than enough accuracy since the errors in our NWChem computations are much larger than this in the density. Using ^{7}Be^{+++} alone as an indicator of the accuracy of a given method is not particularly revealing about how well the method will work for calculating the charge densities of ^{7}Be, ^{7}Be^{+}, and ^{7}Be^{++} because of the intricate correlation effects that are present when two or more electrons are present in an atom. However, it is the only charge density that we can solve for exactly. Furthermore, when it is used in conjunction with other reference values we have found that there does seem to be some correlation to the accuracy of the calculations for the other atoms. It has, therefore, been useful in determining basis sets and functionals for both the SCF and DFT calculations.

For a better test of the accuracy of the many electron systems, we have found some previously published charge densities at the nucleus of Be atoms with which we can compare our results. Almbladh, *et al.*, calculate values for the charge density at the nucleus for neutral Be and Be^{++} which they considered to be exact when compared to HF calculations or DFT local density approximations [41]. Although computational chemistry has improved a great deal since 1983, these calculations are likely still good enough for the preliminary calculations we are presenting here. In any case, these values will at least provide some benchmark of accuracy by which we can ensure that our preliminary calculations are reliable. However, it is plain that a more accurate calculation using modern techniques is needed to verify the findings of these methods and we are currently working on performing CCSD calculations using Molpro.

We next looked for a basis set that would give us the charge densities that were closest to our three reference values. We found that the single most accurate basis set available, short of creating our own basis set, was the uncontracted well-tempered basis set (WTBS). In its uncontracted form, the WTBS basis set contains 20 radial functions and has the tightest functions out of any of the basis sets on the EMSL BSE website. These features make WTBS an ideal basis for our calculations. When doing our SCF calculations we also found that our charge densities could be improved slightly if we augmented this basis set with the angular functions in the aug-pcS-4 basis set. Charge densities calculated using the most accurate basis sets with the tightest functions and most numerous s orbital functions are given in Table 1.

Table 1
Electron densities (in electrons a.u.$^{-3}$) at r=0 calculated for ^{7}Be, ^{7}Be$^+$, ^{7}Be^{++}, and ^{7}Be^{+++} using the SCF method. The "exact" values for ^{7}Be and ^{7}Be^{++} come from Almbladh, *et al.*, [41] and the value for ^{7}Be^{+++} is the hydrogenic charge density (ignoring fine-structure and relativity).

Atom	"Exact"	cc-pCVQZ	Partridge Uncontr. 3	aug-pcS-4	WTBS	WTBS augmented with aug-pcS-4
^{7}Be	35.37	34.724	35.262	35.162	35.293	35.297
^{7}Be$^+$	--	34.417	34.951	34.851	34.981	34.985
^{7}Be^{++}	34.4	33.713	34.236	34.139	34.266	34.269
^{7}Be^{+++}	20.3718	19.989	20.300	20.242	20.317	20.319
Avg. % Error	--	1.901	0.378	0.661	0.292	0.282

On the other hand, our DFT calculations were best when only the WTBS basis set was used. However, in addition to basis sets, DFT calculations require a set of density functionals as well. When looking for the best density functionals, we compared the calculated ionization energies to their known values and again looked at how well the charge densities matched our reference values. While there were quite a few density functionals that produced accurate ionization energies, there were relatively few that could also produce accurate charge densities. In fact, the best results were obtained when we used a class of functionals developed by Haprecht, Cohen, Tozer, and Handy (HCTH) that use the generalized gradient approximation (GGA). A list of the ionization energies and charge densities calculated using the different HCTH functionals is given in Tables 2 and 3 respectively. The HCTH group is fitted to highly accurate experimental data (known as the Gaussian 2 set [42]) for first and second row atoms/molecules on the periodic table as well as accurate exchange-correlation potentials [43]. Although there were some functionals in this group that were very accurate at obtaining our reference charge densities for a particular ion of ^{7}Be, but did not perform as well on the others. Therefore we chose to use the plain HCTH functional because it has better consistency in performing well on all of the atoms. Our three reference charge densities, along with a list of the best charge densities obtained from NWChem using the SCF and DFT methods, are given in Table 4.

Table 2
Ionization energies (in kJ/mol) of ^{7}Be$^+$, ^{7}Be^{++}, and ^{7}Be^{+++} using NWChem's DFT module for the XCTPSSH and HCTH class of functionals. The Exact ionization energies come from Moore [44].

Ionization Energy	Exact	hcth	hcth120	hcth147	hcth407	hcthp14	hcth407p	xctpssh
I_1	899.4	875.05	889.85	887.98	906.56	907.08	914.18	873.58
I_2	2656.5	2644.63	2670.68	2666.51	2681.87	2769.93	2685.04	2647.25
I_3	17504.5	17522.89	17533.60	17531.18	17544.49	17615.65	17547.78	17512.86
Avg. % Error	--	0.788	0.587	0.600	0.660	1.920	0.988	0.857

Table 3
Electron densities (in electrons a.u.$^{-3}$) at r=0 calculated for ^{7}Be, ^{7}Be^{+}, ^{7}Be^{++}, and ^{7}Be^{+++} using NWChem's DFT module for XCTPSSH and HCTH class of functionals. The "exact" values for ^{7}Be and ^{7}Be^{++} come from Almbladh, *et al.*, [41] and the value for ^{7}Be^{+++} is the hydrogenic charge density (ignoring fine-structure and relativity).

Atom	"Exact"	hcth	hcth120	hcth147	hcth407	hcthp14	hcth407p	xctpssh
^{7}Be	35.37	35.385	35.374	35.353	35.333	35.191	35.370	35.436
^{7}Be^{+}	--	35.064	35.051	35.031	35.010	34.865	35.045	35.107
^{7}Be^{++}	34.4	34.365	34.347	34.329	34.314	34.156	34.348	34.406
^{7}Be^{+++}	20.3718	20.301	20.277	20.269	20.267	20.179	20.289	20.156
Avg. % Error	--	0.165	0.211	0.252	0.289	0.721	0.186	0.421

Table 4
Summary of the best electron densities (in electrons a.u.$^{-3}$) at r=0 calculated for ^{7}Be, ^{7}Be^{+}, ^{7}Be^{++}, and ^{7}Be^{+++} using SCF and DFT methods. The "exact" values for ^{7}Be and ^{7}Be^{++} come from Almbladh, *et al.*, [41] and the value for ^{7}Be^{+++} is the hydrogenic charge density (ignoring fine-structure and relativity).

Atom	"Exact"	SCF	DFT
^{7}Be	35.37	35.2965	35.3852
^{7}Be^{+}	--	34.9845	35.1072
^{7}Be^{++}	34.40	34.2689	34.3648
^{7}Be^{+++}	20.3718	20.3193	20.3007

Finally we used these charge densities in equation (8) to acquire relative changes in the decay constant for ^{7}Be^{+} and ^{7}Be^{++} and normalized our neutral decay constant to the proposed decay constant in Das and Ray. This allowed us to plot our results over their data and to analyze what trends can be seen over the entire 2s electron range. Because it was not intuitive as to what model should be used to fit the data we tried a number of different models on both SCF and DFT results: linear, quadratic, cubic, and exponential (Figs. 2–5). For each model we used a weighted fit so that the more accurate data points would carry more importance in determining the shape of the line. We also added a variational parameter in the height of our NWChem results since we do not know the actual decay constant for any of the atoms. By minimizing this parameter in the weighting function we were able find the optimal height for our NWChem results for each model and analyze which model best fits the overall data. There is a caution to consider when sliding two different data sets around in order produce the best fit. This has the potential to *over* fit the data, i.e., produce a fit that is better than reality. However, because the decay constants for ^{7}Be and its ions are currently unknown and both data sets are subject to possible offsets, there is no other option but to normalize our data in this way.

This is not intended to be an exhaustive study on how to model this relationship between decay constant and 2s electrons (although this would be a valuable topic for subsequent research). We are merely trying to demonstrate whether the relationship is linear or non-linear and to ascertain a better value for the decay constant of neutral ^{7}Be. From the graphs in Figures 2 & 4 it seems clear that the relationship is indeed non-linear and appears to most resemble quadratic behavior. In Figure 6 we have plotted the quadratic fit for both the SCF and DFT calculations again and added the linear fit done by Das and Ray. The quadratic model in the region considered by Das and Ray appears to be quite linear and seems to verify their observations for the behavior between about n_e=2.2–2.8. However, there seems to be some non-linear effects that make a linear model insufficient at predicting the behavior of the decay constant over the entire range of 2s electrons.

The cause most suspect for the non-linearity would be interelectron repulsion. Because both 1s and 2s orbitals are spherically symmetric about the nucleus, as the fraction of 2s electrons increased there would be a small amount of repulsion causing the 1s electrons to become more diffuse. Thus even though the overall electron density may increase at the nucleus due to the increase in 2s electrons, there would be a small competing effect to decrease the electron density as well. However, you would expect this to be tied up in the correlation effects of the electrons. Since correlation is not included in the methods

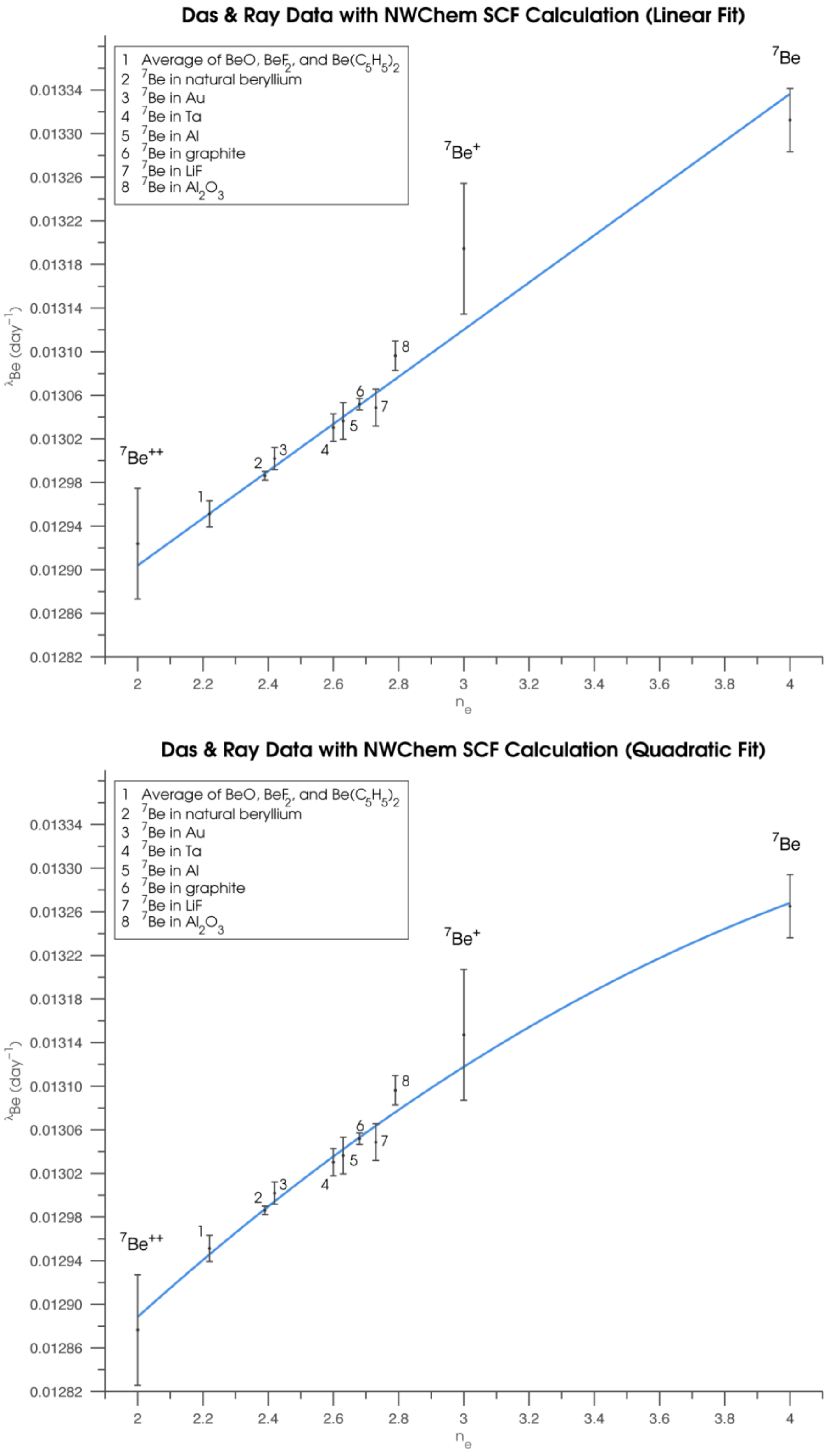
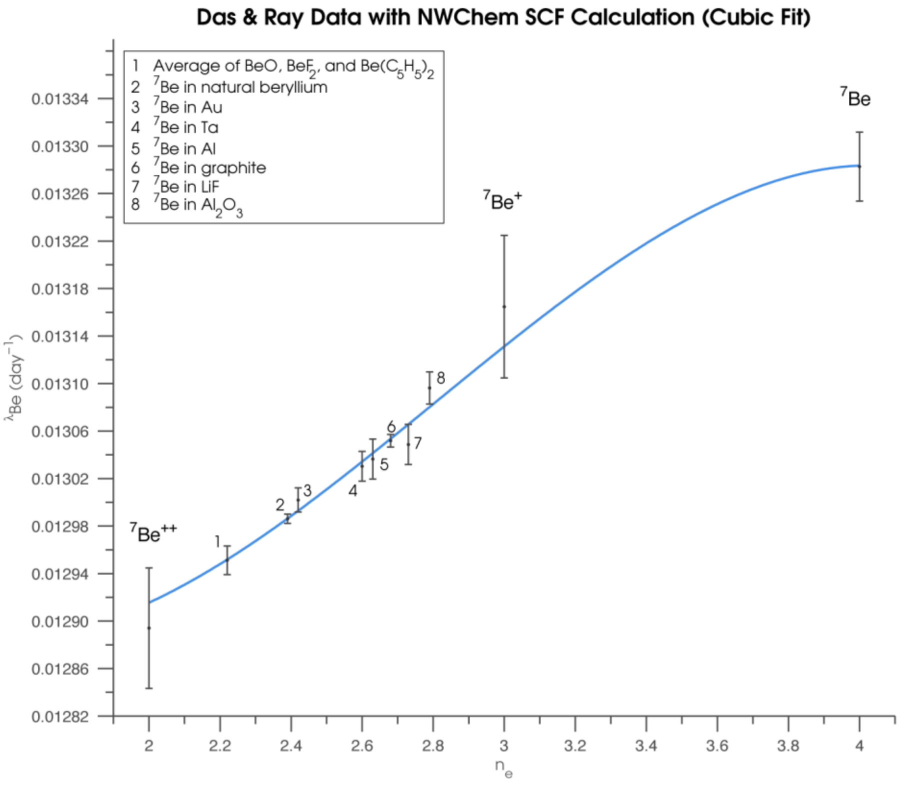
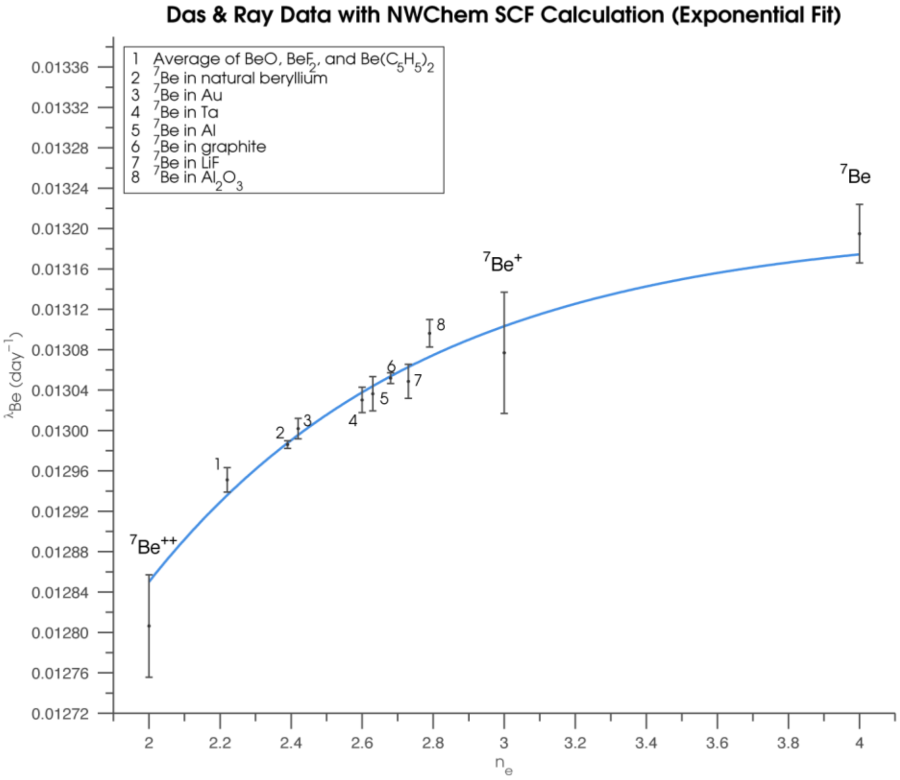


Fig. 2 We have plotted our SCF calculation with Das and Ray's data and performed a weighted fit using a linear and quadratic model. We have also allowed the absolute height of the NWChem calculations to vary while minimizing the error in the fit since we do not know the actual half-life of any of the atoms.

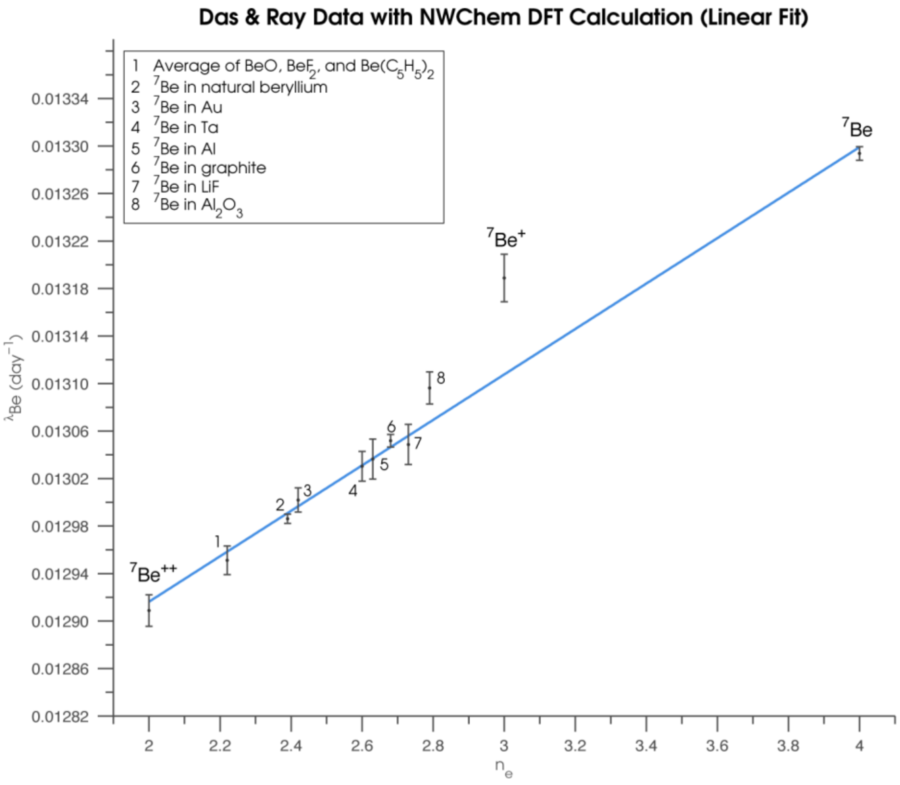


Das & Ray Data with NWChem SCF Calculation (Cubic Fit)



Das & Ray Data with NWChem SCF Calculation (Exponential Fit)

Fig. 3 We have plotted our SCF calculation with Das and Ray's data and performed a weighted fit using a cubic and exponential model. We have also allowed the absolute height of the NWChem calculations to vary while minimizing the error in the fit since we do not know the actual half-life of any of the atoms.


Das & Ray Data with NWChem DFT Calculation (Linear Fit)

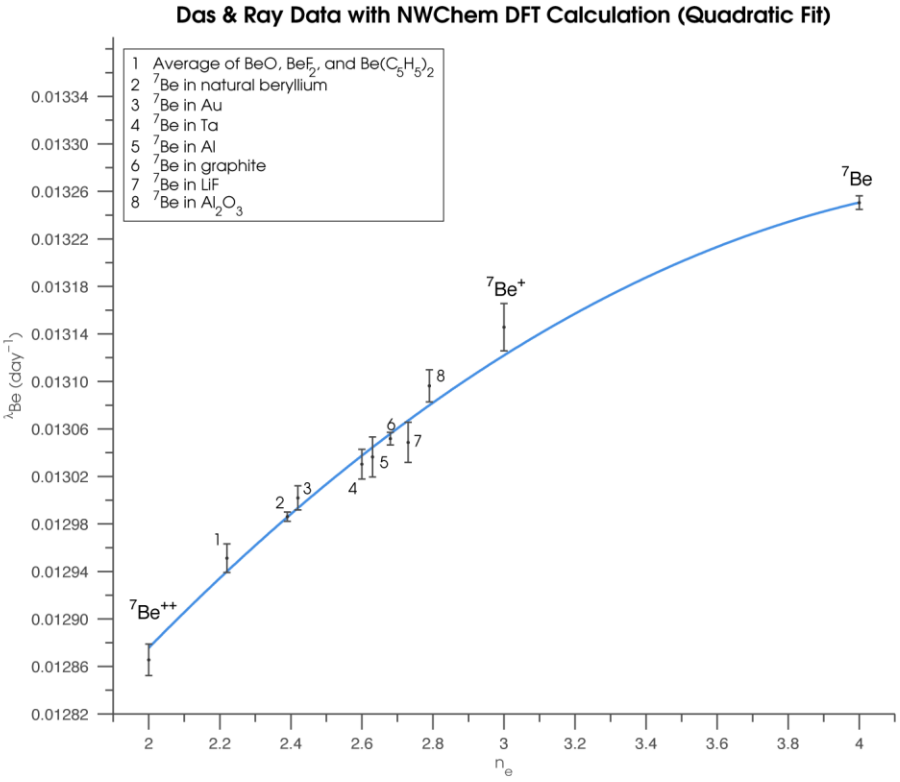

Das & Ray Data with NWChem DFT Calculation (Quadratic Fit)

Fig. 4 We have plotted our DFT calculation with Das and Ray's data and performed a weighted fit using a linear and quadratic model. We have also allowed the absolute height of the NWChem calculations to vary while minimizing the error in the fit since we do not know the actual half-life of any of the atoms.

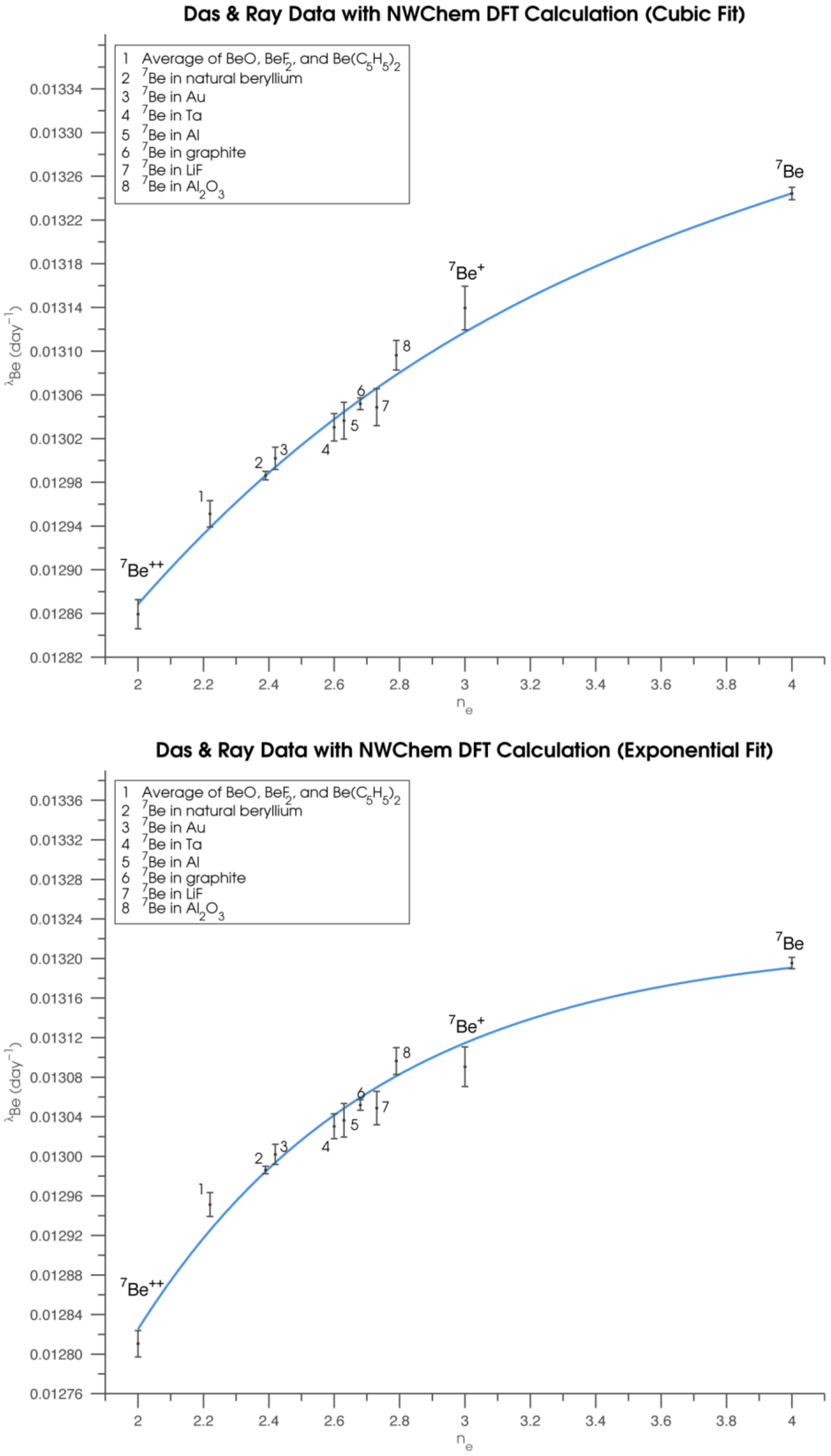


Fig. 5 We have plotted our DFT calculation with Das and Ray's data and performed a weighted fit using a cubic and exponential model. We have also allowed the absolute height of the NWChem calculations to vary while minimizing the error in the fit since we do not know the actual half-life of any of the atoms.

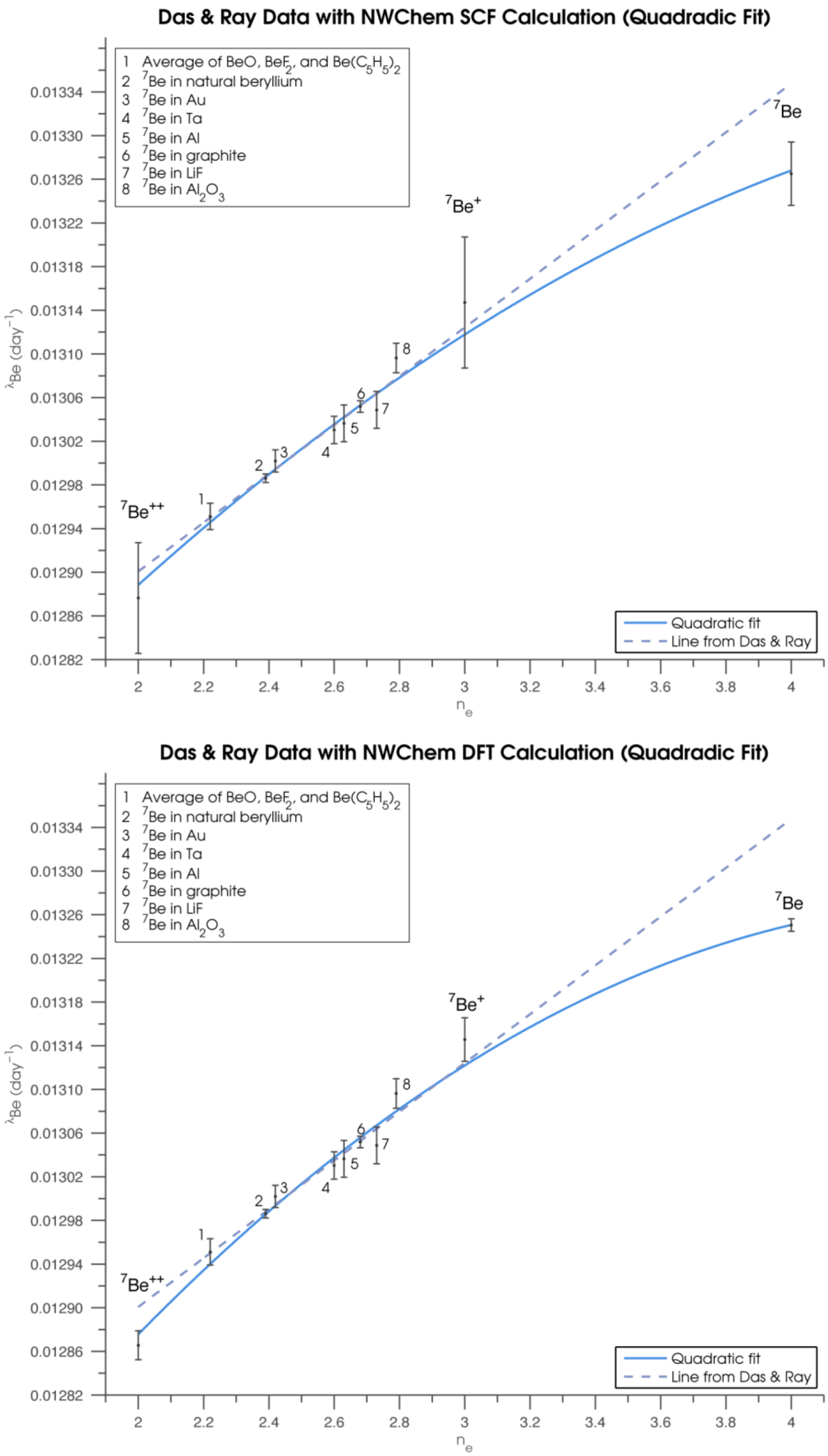


Fig. 6 The quadratic model best seemed to fit the data from both NWChem and Das and Ray. Here we plotted the graphs again and have now included Das and Ray's proposed linear relationship between decay constant and 2s electrons in the atom.

we are using our results are somewhat puzzling. This is another area that should be researched more in depth, but is outside the scope of our present research project.

VI. CONCLUSION

We have performed a SCF and DFT calculation of the electron charge densities at the nucleus of ^{7}Be, ^{7}Be$^+$, ^{7}Be^{++}, and ^{7}Be^{+++} atoms and used these to generate relative changes in the decay constant. When we plot these charge densities with the results of Das and Ray we found a non-linear relationship between the decay constant and the fractional amount of 2s electrons in the atom. This is most likely caused by interelectron repulsion between 1s and 2s electrons. This means that the half-life of neutral ^{7}Be is longer than the predicted half-life given by Das and Ray. Improvement on the decay rate for ^{7}Be will help to reduce the error in the ^{8}B solar neutrino calculation in the SSM and could possibly show whether ionized ^{7}Be could be responsible for the unexpected amounts of beryllium on the LDEF.

It is very important to realize that the calculations and curves generated in this paper are entirely subject to a correct measurement of at least one of the half-lives of ^{7}Be, ^{7}Be$^+$, ^{7}Be^{++}, or ^{7}Be^{+++}. Any one of these measurements will pin down one of the points on the curve and the absolute scaling for our calculations. Thus, if the plasma group at Brigham Young University is successful at measuring a half-life for ^{7}Be$^+$ we will be able to find the actual decay constant for neutral ^{7}Be to a fairly high degree of accuracy. To completely verify these results we suggest that an additional calculation, at least at the CCSD level, be performed in order to take care of the correlation effects of the electrons.

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APPENDIX A

Acronym Glossary

aug-pcS-n	Augmented polarization consistent basis set for nuclear magnetic shielding constants with polarization level n
CC	Coupled cluster
cc-pCVnZ	Correlation consistent polarized core-valence n-tuple zeta basis set
cc-pwCVnZ	Correlation consistent polarized weighted core-valence n-tuple zeta basis set
CCSD	Coupled cluster with single and double excitations
CCSDT	Coupled cluster with single, double, and triple excitations
CCSDTQ	Coupled cluster with single through quadruple excitations
CI	Configuration interaction
DFT	Density functional theory
EMSL	Environmental molecular sciences laboratory
GGA	Generalized gradient approximation
GTO	Gaussian-type orbital
HCTH	GGA exchange-corrlation functional of Hamprecht, Cohen, Tozer, and Handy
HF	Hartree–Fock
LDEF	Long-duration exposure facility
MO	Molecular orbital
MPn	Møller–Plesset perturbation theory of order n
SCF	Self-consistent field
STO	Slater-type orbital
WTBS	Well-tempered basis set
xctpssh	Meta-GGA and hybrid density functional by Tao, Perdew, Staroverov, and Scuseria

APPENDIX B

NWChem Input Files

This is the NWChem input file used to generate the SCF calculations for this paper:

```
Start be

charge 0

geometry units au
  Be 0 0 0  mass 7.016928
end

basis  spherical nosegment
  Be library "uncontracted_WTBS"
  Be library "uncontracted_aug-pcS-4"
end

scf
  singlet
  vectors output Be.movecs
  ROHF
end

dplot
  TITLE DENSITIES
  vectors Be.movecs
  LimitXYZ units au
  -1    1    100000
  -0    0     0
  -0    0     0
  spin total
  gaussian
  output aug0.cube
end

task scf
task dplot
```

This is the NWChem input file used to generate the DFT calculations for this paper:

```
Start be

charge 0

geometry units au
  Be 0 0 0  mass 7.016928
end

basis
  Be library "uncontracted_WTBS"
end

dft
#mult 2
 xc  hcth407p
 vectors output be.movecs
end

dplot
  TITLE DENSITIES
  vectors be.movecs
  LimitXYZ units au
  -1    1    100000
  -0    0     0
  -0    0     0
  spin total
  gaussian
  output corr.cube
end

task dft
task dplot
```

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