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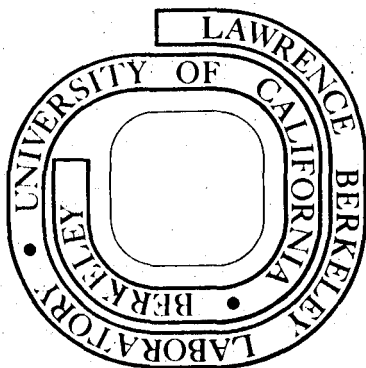
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Electron Correlation in Small Metal Clusters.
Application of a Theory of Self-Consistent Electron Pairs
to the Be₄ System

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Abstract

A knowledge of the properties of small metal particles is essential to the understanding of catalysis on a molecular level. In this regard, one particularly important property is the rate at which the dissociation energy of a small metal cluster approaches the bulk cohesive energy. The present research concerns the effect of electron correlation on the dissociation energy of a particularly stable beryllium cluster, the tetrahedral Be_4 system. A contracted gaussian basis set of size $\text{Be}(9s\ 4p/5s\ 2p)$ was adopted in conjunction with the recently developed theory of self-consistent electron pairs (SCEP). Several new theoretical and computational wrinkles are discussed, including the incorporation of the SCEP/coupled electron pair approximation (SCEP/CEPA). The Be_4 results provide strong evidence for the reliability of the Hartree-Fock approximation for alkaline earth cohesive energies. As suggested earlier the Be_4 dissociation energy appears to be ~ 40 kcal/mole. Analogous studies of the Be_2 molecule are reported.

Introduction

An important recent trend in science is the serious attempt being made¹ to relate surface science,² generally considered basic research, to catalysis,³ traditionally a very applied discipline. One result of the surface chemistry $\rightarrow$ catalysis expedition is an awakening of interest in the properties of small metal clusters.⁴ During the past several years, a number of ab initio theoretical studies⁵⁻¹² of metal clusters have been carried out. On the experimental side a key issue has been the rate at which the dissociation energy of a small metal particle M_n approaches the cohesive energy of the metal with respect to the number of metal atoms n . Perhaps the most fascinating study of this type is the shock tube research of Freund and Bauer¹³ on iron atom clusters. They conclude that the approach to infinite (metallic) behavior is relatively slow, with e.g., the Fe_{100} cluster having only $\sim 65\%$ of the metal's cohesive energy.

In general, one of the most severe challenges for ab initio electronic structure theory has been the reliable prediction of dissociation energies.¹⁴ The best known example is the F_2 molecule, for which the Hartree-Fock approximation predicts no binding at all.¹⁵ However, in our work on beryllium clusters, it was suggested¹⁶ that in certain cases Hartree-Fock theory may be capable of reasonable cohesive energy predictions. For Be_n (and Mg_n , Ca_n , etc.) systems the usual expectancy that there will be more electron correlation for the molecule than the n separated Be atoms may be balanced by an opposing effect. This arises from the fact that the single determinant Hartree-Fock model only allows s basis functions for the $1s^2 2s^2$ electronic ground state. However, as the Be atoms are brought together, p

functions begin to contribute to the molecular wave function, and at the equilibrium geometry, the Be valence shell hybridization is roughly sp. Thus, in a certain sense, the Hartree-Fock wave function actually provides a better description of the Be_n cluster than of the n separated Be atoms. Of course p functions do contribute significantly to the Be atom wave functions but only after configuration interaction (CI) is introduced, most readily by adding the $1s^2 2p^2$ "degeneracy effect" configuration.^{17,18}

Although the above model may appear limited, it is also at least partially applicable to all transition metals with atomic ground electron configurations of the form $s^2 d^n$, e.g. the Mn atom $4s^2 3d^5$. Here again the s-p hybridization is not allowed for the Hartree-Fock atom, but will be qualitatively described in the Hartree-Fock treatment of metal clusters. To the degree to which the metal sp hybridization is involved in the metal clusters, the Hartree-Fock approximation may provide reasonable cohesive energy predictions.

The purpose of the present research was to explicitly test the validity of the Hartree-Fock model in predicting the dissociation energy of a simple metal cluster. Primarily for two reasons the tetrahedral Be_4 system was chosen. First it is the smallest Be_n cluster to exhibit any significant amount of binding. Secondly, Be_4 has been the subject of a previous study¹⁶ at the Hartree-Fock level of theory. The theoretical approach adopted was the recently developed theory of self-consistent electron pairs (SCEP).^{19,20}

Theoretical and Computational Aspects

The theory of self-consistent electron pairs has been presented elsewhere,¹⁹ and representative calculations using the SCEP formalism in its variational form along with a general discussion of the computational features of the method have already been given.²⁰ However, in this report we include the first SCEP calculations using the Coupled Electron Pair Approximation (CEPA) of Meyer,²¹ and thus a brief description of the theory and calculational approach is appropriate.

The form of an SCEP wave function is

$$\psi = \psi_o + \sum_P \psi_P \quad (1)$$

ψ_o is a closed shell reference determinant and ψ_P is a doubly substituted function for an internal pair of electrons, say in the $|i\rangle$ and $|j\rangle$ orbitals (occupied in ψ_o) and singlet ($p = +1$) or triplet coupled ($p = -1$); that is, $P = (ij,p)$ in the notation used here. Each ψ_P implicitly includes all double substitutions of the internal pair P by external or virtual orbitals, such as $|a\rangle$ and $|b\rangle$. ψ_P is then represented as a pair coefficient matrix C_P which is given directly in terms of basis functions. When singly substituted configurations are included, the wave function has the following form

$$\psi_s = \psi_o + \sum_P \psi_P + \sum_{i,a} C_i^a \psi_i^a \quad (2)$$

ψ_i^a is a substitution of the $|i\rangle$ orbital by the $|a\rangle$ virtual orbital and C_i^a is a simple expansion coefficient.

A direct operator formalism is used to achieve an iterative self-consistent solution of the form

$$\langle \psi_p^{ab} | H-E | \psi \rangle = 0 \quad (3)$$

or

$$\langle \psi_1^a | H-E | \psi_s \rangle = 0 \quad (4)$$

where ψ_p^{ab} is a specific substitution of the pair P. The solution of (3) is performed independently of (4). That is, a set of iterations involving only double substitutions are performed to achieve an optimum wave function of the form of (1). This part of the wave function (ψ in ψ_s) is held fixed, except for renormalization (not explicitly performed), and the Hamiltonian matrix including the single substitutions is iteratively diagonalized as a solution to (4). If the doubles iterations were carried to the final convergence limit then the wave function at this point is termed the "fixed- ψ_0 " wave function (see ref. 20) and is nearly equivalent to a singles and doubles CI treatment, except that the very small effect of the singles on the doubles has been neglected. Alternatively to the fixed- ψ_0 treatment, the singly substituted configurations may be approximately absorbed into the reference determinant¹⁹ by modifying the internal orbitals, e.g., $|i\rangle$. Another set of doubles iterations is then performed and so forth. The final result of this type of calculation is a wave function of the form of (1); single substitution configurations have identically zero expansion coefficients since the iterative scheme yields Brueckner orbitals.^{19,22}

The energy of a wave function of the form of (1) is

$$E = E_o + \sum_P \epsilon_P \quad \text{and} \quad E_o = \langle \psi_o | H | \psi_o \rangle \quad (5)$$

where ϵ_P are "pair correlation energies" and are given by

$$\epsilon_P = \langle \psi_o + \psi | H - E_o | \psi_P \rangle / \langle \psi | \psi \rangle \quad (6)$$

The correlation energy contribution of the single substitution configurations for a wave function of the form of (2) is given by

$$\epsilon_s = \sum_{i,a} C_i^a \langle \psi_i^a | H | \psi \rangle / \langle \psi | \psi \rangle \quad (7)$$

Adding ϵ_s to the energy in (5) gives the total energy of ψ_s .

The above expressions are those used for the variational form of the SCEP treatment. However, unlinked cluster effects may be determined approximately, and non-variationally, by using a slightly different operator in (3) and (4) which yields the CEPA treatment.²¹ (The following expressions specifically refer to CEPA-2.) For the doubles iterations the self-consistent solution desired is

$$\langle \psi_P^{ab} | H - E_P | \psi \rangle = 0 \quad (8)$$

where

$$E_P = E_o + \epsilon_P' \quad \text{and} \quad \epsilon_P' = \langle \psi_o + \psi | H - E_o | \psi_P \rangle / (1.0 + \langle \psi_P | \psi_P \rangle) \quad (9)$$

For the single substitutions, we solve

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$$\langle \psi_i^a | H - E_i | \psi_s \rangle = 0 \quad (10)$$

where

$$E_i = E_0 + \epsilon'_P + \epsilon_s \text{ and } P \equiv (ii, 1) \quad (11)$$

It should be noted that the choice of E_i does not affect the final solution, only the convergence, if the sequence of iterations is performed until all singly substituted configurations are absorbed into ψ_0 , i.e., when $C_i^a \rightarrow 0$. However, it will have some small effect on the result of a fixed- ψ_0 calculation.

The SCEP/CEPA calculations can be performed either by iterating to convergence or near convergence with the variational form and then using (8) and (11) to achieve the CEPA self-consistent result or by proceeding directly to the CEPA solution. The CEPA calculations reported here were of the fixed- ψ_0 treatment and so it was easiest to perform separate variational and CEPA calculations. In a comparison of calculations on H_2O ,²⁰ it was shown that the correlation energy difference of the fixed- ψ_0 treatment relative to a singles and doubles CI was less than 0.02% of the correlation energy obtained by CI. It thus seemed reasonable to use fixed- ψ_0 wave functions in the study of Be_4 ; whereas the more critical features of the Be_2 calculations suggested a full sequence of the SCEP treatment, completely absorbing singly substituted configurations into ψ_0 . Since in the Be_4 calculations the singles are not absorbed, there will be a small error in the CEPA result. A measure of this fixed- ψ_0 CEPA error is found by investigating the energies of four Be atoms at large separation.

Exclusive of the error, the CEPA result should be exactly equal to the sum of the variational energies of four isolated Be atoms in an SCEP or CI calculation including single and double excitations from the wave function of each atom. With the double zeta basis set described below, a CEPA fixed- ψ_0 calculation on Be_4 ($R = 100$ a.u.) gave an energy of -58.46619 while four times the variational SCEP energy of a Be atom is -58.46659 . As a percentage of the correlation energy, the fixed- ψ_0 CEPA error is, then, 0.2%. This does not seem to be a serious error but does suggest that more care should be taken in using the fixed- ψ_0 CEPA calculations than fixed- ψ_0 variational results.

We regard the SCEP computer program to be at a somewhat preliminary stage of development with efficiencies continuing to be implemented. Indeed, during the course of calculations reported here the computation time for a Be_4 calculation was reduced by two-thirds. The program currently does not take advantage of symmetry,¹⁹ so in no symmetry the number of configurations required to do an equivalent CI calculation on Be_4 is 10,585. Computation times for Be_4 on the Harris 100 minicomputer were 40 minutes for integrals calculation, up to 20 minutes for SCF, and 7 hours for a fixed- ψ_0 SCEP calculation, with 7 doubles iterations required for convergence to 10^{-6} a.u. and each iteration requiring under 45 minutes (using the most improved program version). CEPA calculations, require no extra operations and thus, the time for one iteration was the same. However, convergence directly to the CEPA result required two more iterations than the variational calculations. The Be_4 calculations at $R = 100$ a.u. required only 15 minutes per iteration or one-third of the time at a small internuclear distance. The reason for

this dramatic difference is that because of the geometry many of the two-electron integrals are negligibly small, say less than 10^{-10} a.u. These small values are not included in the list of two-electron integrals which are processed with SCEP in the construction of various operators. Such a savings from ignoring negligible integrals is difficult to achieve with any conventional CI program because of the requirement of an integrals transformation, which at some intermediate point must include the full integrals list. This advantage of SCEP has been pointed out,²⁰ but Be_4 is a particularly dramatic example.

Be_2 SCEP calculations with the 44 function basis set described below required less than 4 minutes per doubles iteration. Fixed- ψ_0 calculations required up to 50 minutes on the minicomputer.²³ Absorbed singles calculations, which were most often run for Be_2 , varied in computation time, though a typical number was somewhat longer than 2 hours. Convergence was easy to achieve in Be, Be_2 and Be_4 double zeta calculations. With larger basis sets, the low-lying virtual orbitals were better described giving rise to smaller energy denominators used in the first-order perturbation iterative scheme. For these basis sets, an additive constant (see reference 20 for a full discussion) was essential to achieve convergence. This is a special problem only encountered with low-lying virtual orbitals; as such, Be_2 represents a difficult test case for SCEP. Generally, a constant of 0.18 was used and convergence was efficient. The exact choice of the constant is, in fact, not too critical, for tests with constants between 0.12 and 0.25 affected convergence by just a few iterations.

The beryllium s basis set used was the (9s) primitive gaussian set optimized by van Duijneveldt.²⁴ This was contracted (9s/5s) to allow

maximum flexibility in the valence region, i.e., 51111. The p basis was the (4p/2p) contracted gaussian set of Yarkony.²⁵ Thus for Be₄ a total of 84 primitive gaussian functions was reduced to a final set of 44 contracted functions. At the SCF level this basis predicts a binding energy of 33.9 kcal/mole. The Hartree-Fock limit is expected to be close to 40 kcal, the value obtained¹⁶ when a comparable basis is augmented by a set of d functions centered on each Be atom. So it is seen that the basis set adopted accounts for nearly 90% of the estimated Hartree-Fock dissociation energy of Be₄.

Be₄ Results and Discussion

For the Be atom, our (9s 4p/5s 2p) basis yields an SCF energy of -14.57229, in rather close agreement with the Hartree-Fock limit²⁶ -14.57302 hartrees. In all the studies of electron correlation reported here, the Be 1s or core SCF orbitals remain doubly-occupied or frozen. From Bunge's work²⁷ the valence shell correlation energy of Be is about -0.0468 hartrees. Our SCEP calculation yields an atomic energy of -14.61667 hartrees, implying a valence shell correlation energy of 0.04438 hartrees, or 95% of the correlation energy. This is not a particularly surprising result since it is well known^{17,18} that most of the $2s^2$ correlation energy of Be comes from the $2s^2 \rightarrow 2p^2$ configuration. Nevertheless it is encouraging to recover such a large fraction of the valence shell correlation energy.

The present Be₄ results are summarized in Table I. The first point to be made is that, consistent with most other carefully studied molecular systems,¹⁴ correlation increases the predicted Be-Be bond distance. In the present case this increase is 0.018 Å. Since we have shown earlier¹⁶ that the Hartree-Fock limit internuclear separation is ~ 2.08 Å, it is reasonable to add the correlation correction to the latter result and suggest 2.10 Å as the estimated Be-Be bond distance.

The predicted SCEP dissociation energy is 35.5 kcal, or only 1.6 kcal greater than the SCF result obtained with the same basis. At the predicted SCEP equilibrium geometry and at infinite separation (actually $r(\text{Be-Be}) = 100$ bohrs), the SCEP/CEPA procedure described above has been carried out. Although this method^{19,21} does not yield a variational result, it does give a good measure of the importance of unlinked cluster effects. For equilibrium

Be_4 the CEPA estimate of these effects is 0.0295 hartrees, while 0.0335 hartrees is obtained at the dissociation limit. Since the symmetric dissociation of Be_4 is an obvious model case for the importance of unlinked clusters, it is not surprising that these effects slightly decrease the predicted SCEP D_e value. The point to be emphasized is that both SCEP and SCEP/CEPA concur that the Hartree-Fock prediction is essentially correct. In that sense our results are strongly reminiscent of the results of Ahlrichs²⁸ for the lithium hydride dimer.

To aid in a visual picture of the correlation effects, Table II gives the SCEP and SCEP/CEPA pair energies. As discussed earlier^{19,20} the SCEP pair energies are variational in that they sum to yield the total variational SCEP energy. The SCEP/CEPA energies sum to give the nonvariational SCEP/CEPA energy. We first note that the qualitative picture of the different pair energies is the same in the SCEP and CEPA treatments. The only difference is that the CEPA pair energies are uniformly greater in magnitude.

In light of Table II, the "fortuitous" accuracy of the Hartree-Fock approximation in Be_n cohesive energy predictions is readily understood. As expected, formation of Be_4 from the four separated atoms, results in $(16-4) = 12$ new nonvanishing pair energies. Furthermore the magnitudes of the twelve new pair energies are by no means negligible--they sum to 0.1049 hartrees, more than half of the calculated correlation extra. This corresponds to the normal extra-molecular correlation energy for Be_4 . However, Table II also shows that the diagonal pair energies $\epsilon(2a_1, 2a_1)$ and $\epsilon(2t_{2i}, 2t_{2i})$ are much smaller for Be_4 than for four Be atoms. This is for precisely the reason hypothesized in our earlier

paper¹⁶--the availability of Be 2p functions for the molecular SCF wave function for Be₄. That is, after removal of the atomic degeneracy effect,^{17,18} the remaining diagonal molecular pair energies are relatively small. It seems clear that this same argument will be applicable to Mg₄ and to Ca₄ as well.

A Diversion

In the course of this work it was decided to apply comparable methods to the van der Waals bound Be_2 molecule, which should have a dissociation energy somewhat less than 1.2 kcal, the experimental²⁹ D_0 for Mg_2 . With such relatively modest basis sets, one does not expect an accurate description of the Be_2 potential curve in light of previous theoretical studies of systems such as He-He³⁰ and Ne-Ne.³¹ For example, in the He-He system 36% of the well depth may be associated with d functions and 6% with f functions. Since p functions are already accessible in the Hartree-Fock description of Be_2 , one line of reasoning might suggest that as much as 6% of the Be_2 D_e could be due to g functions.³² Nevertheless we proceeded, being particularly intrigued by the prediction of Cade³³ that Be_2 is somewhat bound at the Hartree-Fock level.

More specifically the Hartree-Fock energy of two infinitely separated Be atoms is $2(-14.57302)^{26} = -29.14604$ hartrees. However at $r(\text{Be-Be}) = 8.5$ bohrs, Cade computes $E(\text{SCF}) = -29.14667$ hartrees, a result 0.40 kcal/mole below the separated atom result. Using a variety of gaussian basis sets, we were unable to predict any SCF attraction between two Be atoms, either at $R = 8.5$ or elsewhere. Next a large Slater basis was chosen $\text{Be}(6s\ 4p\ 2d)$, yielding an SCF energy -29.14571 hartrees, or 0.21 kcal above the asymptotic limit. Finally, we evaluated³⁴ the total energy of the wave function reported by Cade and obtained -29.14567 hartrees. We conclude that the Be-Be hartree-Fock potential curve is repulsive near $r = 8.5$ bohrs.

Undaunted by the above results we carried out SCEP calculations on Be_2 using the gaussian basis given in Table III. The s basis is that of Van Duijneveldt, contracted (12s/7s) while the p basis began with the earlier cited (4p/2p) set. Then a more diffuse p function was added and this exponent and the next larger one simultaneously optimized. The d function orbital exponent was optimized in SCEP calculations at $r(\text{Be-Be}) = 7.0$ bohrs. The resulting SCEP potential curve has its minimum at roughly 8.5 bohr internuclear separation. At $R = 8.5$ a total SCF energy of -29.14553 hartrees was found, 0.21 kcal repulsive in agreement with our large Slater basis. The SCEP result of -29.22987 however was weakly bound, by 0.13 kcal relative to the comparable $\text{Be} + \text{Be}$ limit. CEPA calculations at $R = 8.5$ and 30.0 bohrs yield essentially the same binding energy. It seems clear that to obtain a realistic result, say 0.7 kcal for the dissociation energy, a much larger basis set (including perhaps one more d function, two f functions, and one set of g functions) is required. However, the present experience is reported here in the hope that it may be of some use to future investigators.

Concluding Remarks

Perhaps our major conclusion is that the cohesive energies of alkaline earth metal clusters M_n are qualitatively predicted by the single configuration Hartree-Fock approximation. If this conclusion is valid, one can make an interesting estimate of the true dissociation energy of Be_{22} , the largest cluster studied using minimum basis SCF methods.⁹ For Be_{22} the predicted cohesive energy was 22.0 kcal/atom, a result which must be corrected for basis set deficiencies. In the Be_4 system, the comparable minimum basis SCF dissociation energy is $D_e \sim 25$ kcal (or 8.3 kcal/atom), as opposed to the near Hartree-Fock result of ~ 40 kcal. If the same scale factor (1.6) is applied to Be_{22} , the predicted dissociation energy is ~ 35 kcal/mole.

Since 35 kcal is a considerable distance from the metallic cohesive energy³⁵ of 76.5 ± 1.5 kcal, it seems clear that Be_{22} is not a good model of the metal with respect to that particular property. However it is of considerable interest to compare this result with a much simpler empirical model. The latter model assume that the dissociation energy of a particular cluster is directly proportional to the number of nearest neighbors or "bonds". In the hcp metal, each Be atom has 12 nearest neighbors, i.e., there are six "bonds" per Be atoms. However in our Be_{22} cluster there are only 67 "bonds" or 3.05 "bonds" per atom. Thus the empirical model predicts

$$\left(\frac{3.05}{6}\right) (76.5) = 38.8 \text{ kcal} \quad (12)$$

for the Be_{22} dissociation energy. Although the agreement with the theoretical prediction of 35 kcal is by no means perfect, it is good

0 0 0 0 4 5 0 6 5 6 2

-17-

enough to suggest that the model provides a qualitative explanation of the cluster size dependence of the dissociation energy.

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Table I. Summary of results for tetrahedral Be₄. All energies are in hartree atomic units unless otherwise indicated.

Geometry	R(Be-Be)	E(SCF)	E(SCEP)	Correlation Energy	E(CEPA)
SCF optimum	2.096 Å ^o	-58.34322	-58.48923	0.14601	--
SCEP optimum	2.114 Å ^o	-58.34310	-58.48934	0.14624	-58.51884 ^a
Separated atoms	∞	-52.28915	-58.43270	0.14355	-58.46619
ΔE(Be ₄ → 4Be) (kcal/mole)	--	33.9	35.5	--	33.0

^a The SCEP/CEPA-2 calculation was performed at R(Be-Be) = 2.114 Å^o, the predicted internuclear separation from the variational SCEP procedure.

Table II. Pair energies (in hartree atomic units) for Be_4 at its equilibrium geometry and separated atom limit.

Pair	Spin Coupling	R = 2.114 Å ^o		R = 100 bohr	
		SCEP	CEPA	SCEP	CEPA
(2a ₁ , 2a ₁)	singlet	-0.0059	-0.0069	-0.0357	-0.0439
(2a ₁ , 2t ₂) ^a	singlet	-0.0200	-0.0237	0.0000	0.0000
	triplet	-0.0108	-0.0125	0.0000	0.0000
(2t _{2i} , 2t _{2i}) ^b	singlet	-0.0491	-0.0595	-0.1070	-0.1318
(2t _{2i} , 2t _{2j}) ^c	singlet	-0.0298	-0.0370	0.0000	0.0000
	triplet	-0.0286	-0.0317	0.0000	0.0000
$\Sigma \epsilon_p$		-0.1442	-0.1713	-0.1427	-0.1758
Single excitations		-0.0021	-0.0044	-0.0009	-0.0013
Correlation energy		-0.1463	-0.1757	-0.1435	-0.1770

^a These "pair energies" are each the sum of three results, i.e., [(2a₁, 2t_{gx}) + (2a₁, 2t_{gy}) + (2a₁, 2t_{gz})].

^b Sum of [(2t_{gx}, 2t_{gx}) + (2t_{gy}, 2t_{gy}) + (2t_{gz}, 2t_{gz})].

^c Sum of [(2t_{gx}, 2t_{gy}) + (2t_{gx}, 2t_{gz}) + (2t_{gy}, 2t_{gz})].

Table III. Beryllium atom contracted gaussian basis set for use in the Be_2 molecule electronic ground state.

Type	Exponent α	Contraction Coefficient
1s	11781.69	0.000 120
1s	1760.98	0.000 939
1s	398.404	0.004 951
1s	111.638	0.020 723
1s	35.8247	0.070 838
1s	12.7216	0.186 700
1s	4.87486	1.0
1s	1.967 869	1.0
1s	0.830 394	1.0
1s	0.258 705	1.0
1s	0.106 756	1.0
1s	0.043 102	1.0
2p	3.202	0.052 912
2p	0.6923	0.267 659
2p	0.2016	0.792 085
2p	0.1183	1.0
2p	0.0694	1.0
3d	0.19958	1.0

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