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ELECTRONIC ENERGIES FOR NEON DIMER
DICATION RADIATIVE CHARGE TRANSFER

THESIS

Roger Alan Deemer
Captain, USAF

AFIT/GEP/ENP/89D-1

DEPARTMENT OF THE AIR FORCE

AIR UNIVERSITY

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Wright-Patterson Air Force Base, Ohio

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THESIS

Presented to the Faculty of the School of Engineering

of the Air Force Institute of Technology

Air University

In Partial Fulfillment of the

Requirements for the Degree of

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Roger Alan Deemer, B.S
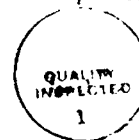
Captain, USAF

December, 1989

Preface

This research was conducted to find the shape of the potential energy surfaces for the Neon dimer dication, designated Ne_2^{+2}, to include all symmetries which dissociate to two ground state Ne^+ ions or a ground state Ne atom and Ne^{+2} ion. The motivation is to investigate whether there is a minimum in the upper level, the Ne^{+2} and Ne level, located in such a way that populations of bound dimer molecules can be built up without dissociating or transitioning to the lower level other than by radiative charge transfer. It is also of interest to show that the ground state is dissociative, that is that its energy is monotonically decreasing with increasing nuclear separation.

Calculations were completed using programs known as Gaussian-86, and Diatom. Gaussian-86 results are of limited value since they produce only ground state energies. Diatom produced excellent results for the He_2^{+2} test case. Ne_2^{+2} calculations were not as accurate as He_2^{+2}, but results did indicate that bound upper level states exist which can only undergo charge transfer radiatively.

Without the assistance I received in this effort I would have accomplished very little. I would like to thank my faculty advisor, Captain Haaland, for the many hours he put in getting the computer code running properly and teaching me how to use it, and for his patience in listening to my problems, helping me when he could, and encouraging me every step of the way. A big thanks is also due to Harvey Michels for giving us a copy of the Diatom code and answering numerous questions about running it. I'm grateful to Lt Col Lupo for his help with installing Diatom on the ELXSI computer, and Dr Bailey for answering occasional questions and showing interest in my work. Finally, I am deeply indebted to my wife, Amanda, for her assistance in proof- reading, typing. keeping me company, encouraging me. being patient during my long hours at the computer, but most of all for her faithfulness and love.

Roger Alan Deemer

ii

Table of Contents

List of Tables

Abstract

This research computed Neon dimer dication potential energies for nuclear separations from 0.9 to 20 a.u. of Ne_2^{+2}. Σ, Π, and Δ states are considered which dissociate to two Ne^+ atoms in their ground state, or to the Ne atom and Ne^{+2} ion in their ground states. The purpose of examining these characteristics is to demonstrate that the charge transfer reaction is primarily radiative

$$Ne^{+2} + Ne \longrightarrow Ne^+ + Ne^+ + h\nu$$

Electronic structure calculations indicate that Ne^{+2} should bind with Ne to form Ne_2^{+2*} Once the molecule relaxes by collisions with third particles it should remain in this bound state near 4 a.u. nuclear separation until it can transition to the lower level by radiative charge transfer. Such a process would emit electromagnetic radiation with 0.677 a.u. (18.43 eV) energy.

The ground state is shown to be dissociative over the entire range of nuclear separations considered, a beneficial condition for excimer laser media.

Results for a Helium test case are also presented. Atomic Helium's first 8 energy levels were calculated to within a few mili-Hartrees (mH) of experimentally determined values. Energy surfaces for He_2^{+2} agreed with Cohen and Bardsley's[1] results to within a few mH.

ELECTRONIC ENERGIES FOR NEON DIMER

DICATION RADIATIVE CHARGE TRANSFER

I. Introduction

This report investigates electronic properties of the Neon dimer dication which will be helpful in analyzing its usefulness as an excimer lasing medium operating in the vacuum ultraviolet near 64 nm. The frequency of 4.684×10^{15} Hz could carry extremely high data rates, an order of magnitude above visible wavelengths. With the large energy of individual photons (18.4 eV, 5 times the photon energy of any current operating laser system) there may be high power applications also. The report presents potential energies for various molecular states of Ne_2^{+2} over a region of nuclear separation, R, from .9 to 20 a.u. and discusses the implications of those results. All molecular states are considered which correlate, in the limit of large R, to the atomic ground states of two Ne^+, or Ne and Ne^{+2}. States correlating to two Ne^+ are referred to as lower level states, and those correlating to Ne and Ne^{+2} as upper level states.

Two different computer programs called Gaussian 86, and Diatom were used. Gaussian 86 uses Gaussian functions, which model electron orbitals as wave packets shaped by $\exp(-gr^2)$. g is referred to as the Gaussian orbital exponent. Slater functions more accurately model electron orbitals using wave functions shaped by $\exp(-sr)$ with s being the Slater orbital exponent. Gaussian functions are more commonly used because they are easy to integrate.

A large orbital exponent produces a very sharp peak at r=0 in the orbital wave function. Low energy orbitals in a molecule or atom are compact. That is, the electrons are found very close to the nucleus. Thus lower energy orbitals are modeled with larger orbital exponents. Excited states will have diffuse orbitals, with smaller exponents than ground state orbitals. Possitive ions

1

of increasing ionicity will have larger orbital exponents since the greater nuclear attraction causes electron orbital. be more compact.

Diatom uses Slater orbitals but simplifies the integration process using diatomic symmetry properties. Diatom also computes electronically excited state energies while Gaussian-80 only produces ground state energies.

Both programs use a fixed number of wave functions, selected by the user and referred to as a basis set, to carry out their computations. The accuracy of the final results depends heavily on the choice of basis functions, the orbital types, (1s, 2s, 2p, 2p+, 2p-, etc.) and the values of the orbital exponents. From the variational principle it is known that the most accurate calculation is the one producing the lowest energy.

First a description of some related research that has been published in the past will be given followed by discussion of the computer codes, along with a brief mention of mathematical principles used for calculations.

The majority of this work was consumed by efforts to find a suitable basis set. The computation section will describe that process, the steps involved in selecting basis set orbitals, optimizing Slater exponents, and restricting configurations in the computer calculations. Some difficulties with the computer code will also be discussed.

After a theoretical sketch of the physics behind the problem, results for a completely analogous Helium test case will be presented, followed by Neon atomic calculations, and Ne_2^{+2} calculations. Finally recommendations for further research will be made, and conclusions summarized.

II. Background

Cohen and Bardsley[1] were the first to computationally characterize the charge transfer process of a doubly charged rare gas dimer. In 1978 they computed the potential energies for the He_2^{+2} ground state and first electronic excitation. They also computed dipole transition matrix elements from which Einstein A coefficients were found at various nuclear separations by the relation

$$A = (3g/4c^3)(E)^3 \|U\|^2$$

where g = degeneracy, c = the speed of light, E = energy difference between states, and U = the transition matrix element.[1]

That same year Johnsen and Biondi[2] conducted drift tube experiments for all rare gas elements, measuring the mobility of Rg^{+2} in Rg. Their Helium results agreed with Cohen and Bardsley's.

Ne_2^{+2} has 18 electrons, nine times as many as He_2^{+2}. As one would guess, much more accurate calculations are available for Helium dimers than for Neon. Enrico Clementi used a large basis set (two 1s, four 2s, and twelve 2p functions) of Slater orbitals to compute atomic Neon energies as low as -128.5470 using a Hartre Fock (HF) Self Consistent Field (SCF) method.[3] Just last year T. H. Dunning published results for the Neon atom using 20 Gaussian functions and achieving a ground state energy of -128.833.[4] The literature also reveals a considerable amount of computational and experimental work on neutral and singly charged Neon dimers.[5-9] The most helpful was Cohen and Schneider's paper on Ne_2 and Ne^{+2}.[5] They used Slater functions to compute Ne^+, Ne^{+2}, and Ne_2 potential energies. In all this research, which included a computer literature search, no work was found on the dimer dication, Ne_2^{+2}.

III. Computations

3.1 Computer Code

Diatom is a versatile Fortran code designed uniquely for diatomic molecular electronic structure calculations. It can also be used for atomic calculations. Diatom uses Slater functions to model atomic orbital wave functions. It employs the variational principle that any energy calculated will be greater than or equal to the ground state energy of a system. Wave functions are solutions to the nonrelativistic, time independent Schrodinger Equation resulting from the Born-Oppenheimer approximation that the position of the nuclei are fixed relative to the rapid motion of the electron orbitals.

Given a set of Slater parameters, Diatom creates linear combinations of wave functions to minimize the total energy. Wave functions are combined in what are known as Slater Determinants, which include both spin and space functions, in such a way that they are anti-symmetric with respect to electron exchange. This requirement arises from the Pauli exclusion principle. Diatom uses multiple Slater determinants in forming Hartree Fock (HF) and Configuration Interaction (CI) matrices which, in turn, give multiple eigenvalues. Those eigenvalues are electronic energies of the molecule. Gaussian-86 is restricted to a single energy by its method of forming a single Slater determinant.

Once a minimum is found, the resulting wave functions can be used to compute expectation values for dipole moments or other quantum mechanical operators. The dipole moment expectation value computed at a single state, expressed as $< A|ex|A >$ where ex is charge times position, gives the dipole moment of that state. The same operator applied between two different states gives the dipole transition moment between those states. For example, $< A|ex|B >$ is the transition moment in the x direction between states A and B.

Diatom uses Configuration Interaction (CI) as described in Szabo and Ostlund's Modern Quantum Chemistry to calculate molecular or atomic energies, or it can simply carry out a Self

Consistent Field (SCF) Hartree Fock (HF) computation. For further details on Diatom's approach see the various articles by Michels, Hobbs, Wright, or Connolly.[10,11]

Since full CI, which considers all possible permutations of the basis set, is computationally prohibitive except in systems with only a few electrons, Diatom must be restricted by fixing lowest lying pairs of electrons. This frozen inner core is configured so that it has no contribution to the spin or angular momentum quantum numbers. In other words, the frozen core is a singlet Σ (or singlet S in atomic calculations) so that the final state is determined by the unfixed electrons. These frozen orbitals are modeled by single basis set elements instead of a linear combination of elements.

By specifying the multiplicity, angular momentum quantization, and symmetry, the number of configurations is reduced even further. Diatom can also limit the CI configurations to only those which differ from the ground state by less than a fixed number of orbitals.

To understand the extent of these limitations consider the $^3\Sigma$ state of Ne_2^{+2} with a 1s - 3s basis set. The total number of configurations possible for an 18 electron system with 12 basis orbitals is determined by the binomial formula

$$\frac{(2k)!}{n!(2k-n)!}$$

where k is the number of non-frozen orbitals and n is the number of non-frozen electrons. Substituting k = 12 and n = 18 gives 134,596 possible combinations. By specifying the state as $^3\Sigma$ Diatom needs only 2088 configurations. Freezing the 1s orbitals decreases this number to 308. By freezing the 2s orbitals for a total of 4 frozen core orbitals it's down to 160. Finally by specifying g symmetry Diatom carries out the CI calculation with only 72 configurations. These values increase dramatically with k. For example, adding a set of 6 3p basis orbitals the number of configurations increases from 72 to 4678.

Diatom uses atomic Slater functions to model molecular orbitals. These are input as part of a complex input file that also specifies many other options of the code.

Gaussian-86 is a versatile program that uses similar mathematical principles as Diatom with Gaussian functions instead of Slater functions. Gaussian functions don't model electron orbitals as well, but, since they are much easier to integrate, much larger basis sets can be used. Gaussian-86 has a large number of standard basis sets, of which the 6-311G** proved to give the best results for both Neon and Helium.

Gaussian-86 can compute electronic energies using a variety of techniques. It does HF calculations, CI calculations using single excitations, single and double excitations, up to quadruple excitations, and several different levels of perturbation calculations. The limitation of Gaussian-86 that forced me to use Diatom for this research was that it does not compute excited states, or transition moments, while Diatom can do both.

3.2   Basis Set Optimization

Finding a suitable basis set consumed more time in this effort than all other tasks combined (except, possibly, debugging the code.) Several different methods to produce a good basis set were attempted with varying degrees of success.

First the Slater exponents were varied over a large range to locate energy minima for atomic Neon. By calculating the energy over points closer together the energy was minimized varying one exponent at a time. This process was very slow and each time the Slater exponent for one basis orbital was changed, it changed the location of the energy minima with respect to the other orbital exponents. After several days of work the Neon atomic energy was reduced to just under -120 a.u., far short of the -128.7 value calculated by Gaussian-86 using the 6-311G** basis. About this time Harvey Michels, one of Diatom's authors at United Technologies, explained how to optimize exponents using the code by simply specifying which energy to minimize and which orbitals to

vary in a section of the input file. Also a MATHCAD template was developed to fit Slater curves to Gaussians. Using Gaussian functions from the literature for Helium (and then Neon) Slater functions were matched to them. Then the exponents were optimized. Appendix B describes this process giving a few examples.

The literature contained only ground state Gaussian exponents. Higher level orbital exponents were developed by adding the orbitals to the basis set with exponents roughly 20% less than that of the nearest lower orbital. These higher level orbital exponents were then optimized to minimize a corresponding excited state energy. After optimization higher level basis exponents were usually reduced even further.

An attempt was made to reproduce Cohen and Bardsley's[1] Helium results. This much simpler dimer dication made a good test case to develop an approach to solving the problem, learn how to use the computer code, and verify the code's accuracy.

A 16 element basis consisting of all orbital types from 1s to 4p produced atomic energies whose spacing agreed with spectroscopic values for the first 7 excited states of Helium within 1 or 2 mH (mili-Hartrees). The ground state computed by this basis was over 50 mH high, and all the excited state energies were shifted up by nearly 40 mH. This basis is the He* basis in Table 1.

A significant discovery from the Helium test case was that the ground state energy could be minimized by using larger exponents for higher level basis orbitals. These exponents did not describe the atomic excited states well, but they were very effective in reducing the ground state energy. This makes sense since all basis orbitals are used to modify the solution. In the ground state solution orbital exponents are large since the electron orbits are compact. Higher level basis orbitals with large exponents will modify the ground state better than ones with small exponents. When considering electronic excitations there are diffuse, loosely bound orbitals in the solution which can only be modeled by wave functions with small exponents.

Table 1. Slater Exponents Used in Helium Basis Sets

He* Basis: Gave good values for first 8 energy levels of the Helium atom.			
1s=1.2990	2s=0.4357	3s=0.2985	4s=0.2220
1s$'$=2.4374	2p=0.4711	3p=0.2750	4p=0.2150
		3d=0.3780	
He$_{GS}$ Basis: Gave a lower ground state energy than the He* basis but did not produce accurate values for any electronic excitations. This basis did give reasonable values for the He$_2^{+2}$ ground state and first excited state.			
1s=1.9700	2s=2.0900	3s=2.1800	4s=4.1619
	2p=2.9300	3p=2.9300	4p=2.5463
		3d=3.6100	
He$_2^{+2}$ basis: Gave the best results for all calculations but took a lot longer than either of the above basis sets. This basis produced values for the curves shown in Figures 1 through 5.			
1s=1.9700	2s=2.0900	3s=2.1800	4s=4.1619
	2s$'$=0.4357	3s$'$=0.2985	4s$'$=0.2220
	2p=2.9300	3p=2.9300	4p=2.5463
	2p$'$=0.4711	3p$'$=0.2750	4p$'$=0.2150
		3d=3.6100	
		3d$'$=0.3780	

Eventually these two basis sets were combined. Table 1 displays the optimized exponents of various basis sets.

Extending the basis sets to molecular calculations the basis producing the most accurate excited atomic energies did not model the He_2^{+2} energies well. In fact, as nuclear separation increased, the He_2^{+2} ground state energy approached -2.9 a.u., the energy that the first excited state should approach, which is also the energy of the He atom ground state. This is not surprising since the He_2^{+2} first excited state dissociates to a He atom and an alpha particle with zero energy in the limit of large nuclear separation. A basis set that models the He atom well with no orbitals for a He^+ ion will not map the He_2^{+2} ground state well since it dissociates to two He^+ ions.

The basis set optimized to the best ground state of Helium, with no regard to the excited states, gave very good results for He_2^{+2}. This basis had many compact orbitals without all the diffuse orbitals in the other basis set. This basis mapped the ground state to within a mH of Cohen and Bardsley's results,[1] and was better than the best Gaussian-86 results at all points, but it was as much as 8 mH above Cohen and Bardsley's upper level energies at small nuclear separations. All three energy surfaces of these calculations correspond to ground state atomic species requiring large exponents.

Optimizing 4s and 4p orbital exponents to minimize the first Σ_u state at a separation of 1.3 a.u. improved all three energy surfaces over all nuclear separations. Diatom even gave energies lower than Cohen and Bardsley's at small nuclear separations. This is the He_{GS} basis shown in Table 1.

Finally, the two basis sets were combined by adding the diffuse 2s-4p functions from the He^* basis set to the one optimized for the ground state. This combined set of 62 orbitals gave the most accurate results for both atomic and dimer calculations.

Helium only has 1s orbitals in it's ground state, and the dimer dication only has 1s orbitals in the dissociated limit for all three states considered in this research. Neon however has 5 different

Table 2. Change In Total Electronic Energy in a.u. With Addition of Basis Orbitals

Number of He	Lower Level	Upper Level	
Basis Elements	Σ_g	Σ_g	Σ_u
2 (1s)	-3.79911	-2.76782	-2.76784
4 (+ 2s)	-3.80000	-2.84410	-2.84412
6 (+ 2p_o)	-3.80020	-2.85204	-2.85206
10 (+ 2p_{+1})	-3.80020	-2.86584	-2.86586
12 (+ 3s)	-3.80021	-2.89586	-2.89588
24 (+ 3p,3d)	-3.80040	-2.90152	-2.90156
32 (+ 4s,4p)	-3.80047	-2.90446	-2.90452
62 (+ 2s' − 4p')	-3.80047	-2.90552	-2.90557
Computations at R = 5			

types of orbits, 1s. 2s, 2p_o, 2p_{+1}, and 2p_{-1}. One expects that a good Neon basis would be much more difficult to obtain, and results of the same accuracy may not be achievable. This turned out to be the case in this research. More basis functions were needed to accurately model the true system, but fewer could be used since the number of integrals computed, the number of iterations to achieve convergence, and the size of arrays all increase dramatically with the number of electrons and the number of basis functions.

Accuracy is difficult to quantify in a basis set. Quantities such as ionization energy or polarizability can be computed and compared to experimental values, but sometimes one quantity will agree very closely while another has significant error. Since potential energies are the focus of this research, the best measure of a basis set's usefulness is the energy computed from it. The variational principle dictates that the best basis is the one with the lowest energy values.

To illustrate how accuracy improves with the basis set size, consider the He_2^{+2} Σ energies shown in Table 2. Initially adding basis elements improves the energy considerably, but the closer the energy approaches the true value, the more elements must be added to lower the computed value.

Diatom came with an optimization option which adjusted specified Slater orbitals to minimize the computed energy of the ground state or any excited state. In developing Neon exponents Slater

10

functions could not be fit to all the Gaussian functions in the literature. Instead, Slater exponents from the literature[3,5] for Neon atomic and neutral dimer calculations were optimized. With the total number of configurations limited to 1000, these optimization runs could exceed two days on the ELXSI computer, and took even longer on the MICROVAX, even with no other users competing for CPU time.

Under the 1000 configuration limit the largest useful atomic basis set had a frozen core of 1s and 2s orbitals, a valence level of 2p and 2p' orbitals, and 3s and 3p excited orbitals. This worked somewhat successfully for Ne, and Ne$^+$ calculations because only 12 basis functions were needed, one for each s level and 3 for each p level. Ground state energies were -128.581 a.u. and -127.819 compared to exact values of -129.047 and -128.025 for Ne and Ne$^+$ respectively.[12] Ne$_2^{+2}$ was much more difficult. Dimer calculations require two basis elements for each orbital type, so a dimer basis is twice as large as an atomic basis. Using the same exponents as with Ne$^+$, Diatom needed 24 basis functions with 18 electrons. From the binomial formula there are 1.134×10^{11} configurations possible with 4 core orbitals frozen. Even with restrictions on multiplicity, quantum number, and symmetry, there were still well over 1000 configurations. Limiting the number of excitations proved somewhat successful, but there are some problems with this portion of the program.

Since Ne orbitals will, in general, be more diffuse than Ne$^+$, and Ne^{+2} will be less diffuse, the exponents of the Ne$^+$ Slater functions should lie between those for Ne and Ne^{+2}. A basis set with separate exponents for all three would be too large. The exponents were first optimized for Ne$^+$, because it's in between the others, then used to compute energies of Ne and Ne^{+2}. Exponents for Ne and Ne^{+2} were later optimized independently to see how much the exponents and energies changed, which can be seen by comparing values in Appendix A. Appendix A also lists results of atomic calculations from Gaussian-86 for comparison of ground state energies.

It was not always possible to predict which Neon species would be the most compact in a given orbital. The Ne$^+$ 1s orbital with a Slater exponent of 9.6353 was actually more diffuse than

the Ne 1s with a Slater exponent of 9.6414. Its 2s and 2p orbitals were, however, much more compact, with exponents of 2s = 2.9770, $2p_o$ = 3.1091, and $2p_1$ = 3.0668 versus 2s = 2.8870, $2p_o$ = 2.8800, $2p_1$ = 2.8801 for Ne.

This trend continued for Ne^{+2}. With a nuclear charge of 10 and electron charge of only 8 it would be expected to have the most compact orbitals, but the 1s orbital was actually more diffuse with an exponent of 9.6289. This looser bound 1s orbital was compensated for by the larger 2s and 2p orbital exponents, 2s = 3.0675, $2p_o$ = 3.2514, $2p_1$ = 3.3077.

Many reoptimizations of the exponents were required to realize the above phenomenon. It illustrates the need for optimization and the difficulty of obtaining exponents. No set of rules or procedures exists to produce optimum exponents. Rather, one can only look for values from the literature, trends in their own optimizations, and practice a little trial and error. The process of optimizing and reoptimizing is similar to solving a difficult puzzle where one can see progress, but does not know where to look for the next piece or how long it will take to find it.

When using a single Slater basis function for each orbital, Diatom calculated energies above literature values and Gaussian-86 values. Using two functions for each ground state orbital, one exponent above the single function value and one below, significantly improved those energies. Such a basis is known as double zeta.

Adding extra 1s, 2s, and 2p functions, each one at a time, revealed that the 2p functions had the greatest impact, improving the Ne^+ ground state by 463 mH, Ne^{+2} by 294 mH and Ne by 801 mH. 1s orbitals had the next largest impact decreasing ground state energies by 58, 71, and 46 mH for Ne^+, Ne^{+2}, and Ne respectively. Making the 2s orbital double zeta had the least impact, only changing ground state energies of the three atomic species by 19, 41, and 14 mH.

There are two major aspects of this research that were limited by difficulties with the code. Several problems prevented expansion of the basis sets which was needed to improve the accuracy of Ne_2^{+2} energy computations. The second pitfall was that transition moment calculations never worked for either Neon or Helium.

Using all three basis sets of Table 1 transition moments from both upper levels to the ground state were computed. The results were obviously incorrect. The Σ_g to Σ_g transition moment should have been zero, but Diatom computed values as large as -0.788 a.u. Values for the Σ_u to Σ_g transition ranged from -0.684 to 0.538. From one basis set to the next results were completely different. The only noticeable trend was that values got larger for increasing R, when they should have been getting smaller.

Repeating the run restricted to g states only gave zero for all transition moments as expected. Inputting dual configuration cards to separate the g states from the u states failed because the code would not accept that input. The only way to compute the u to g transition is to leave the symmetry unspecified, and this method gives erroneous data.

One other problem that affected both Helium and Neon molecular calculations was a tendency in the code to find additional roots with extremely large negative energies when using large basis sets at longer nuclear separations. This was not a problem for the 12 element, 1s - 3s, basis used in Ne_2^{+2} calculations which successfully computed energies out to 20 a.u., but when a set of 3p functions was added Diatom could not compute energies for R greater than 8 a.u. The same was true for He_2^{+2} except it could usually go a couple a.u. higher separation before the large negative roots took over. This research is concerned primarily with energies at smaller R. Any basis set which could be used to compute energies out to 6 a.u. was considered adequate.

Three anomalies appeared in the Neon results that did not affect Helium. The first of these was with HF SCF calculations. Attempts to reproduce the results of Clementi, Roothaan, and

13

Yoshimine[3] succeeded only for small systems. Diatom calculated their Lithium ground state to 4 decimal places. but it was 86 mH high on Carbon. Oxygen was half a Hartree high and Neon was 1.35 a.u. high. Diatom computed a Neon HF energy of -127.196 with the same exponents that Clementi and associates computed -128.547 a.u.

Diatom was computing energies lower than the final value (as low as -200 a.u. for Neon) and rising before converging on an answer. This is very curious behavior for a variational calculation which was observed on the ELXSI system but not on the MICROVAX. The MICROVAX used double precision which may indicate the negative initial energies are due to round-off error. Both systems converged to the same SCF result indicating that the error is only significant when the solution used is far from the true solution. The other anomalies may be related to the poor SCF calculation since the HF SCF ground state is used in the CI calculation.

When running a CI calculation which uses a large number of configurations (over 400) Diatom uses a less accurate numerical technique known by the name Shavitt, which is faster. Using more configurations improved the energy values. but the method often returned the energy levels in the wrong order. With fewer configurations Diatom uses the slower, Givens method.

The last major problem in the code is in the way it generates configurations. In atomic calculations the basis set could be optimized without restricting the number of allowed excitations. This way all configurations which matched the specifications on quantum number, multiplicity. and symmetry were included.

The best basis sets were double zeta, that is, they had two functions for each ground state orbital. one with a high exponent and one with a low one. When the number of basis functions were increased to the point of needing further restrictions on the number of configurations, which was the case for all Ne_2^{+2} basis sets larger than 10 elements, the energies increased dramatically. Freezing core orbitals restricted them from being modified by the second basis function, eliminating the advantage of a double zeta basis and making the results worse than with single basis functions.

14

Restricting the number of excitations should have been the answer to this difficulty, but that introduced another problem.

Diatom checks the quantum numbers of the basis functions to determine which configurations differ from the ground state within the restricted number. In doing this it fills all lower level orbitals before filling the valence level, so that the true $1s^2$, $2s^2$, $2p^5$, Ne^+ ground state looks like a quadruple excitation instead. It selects $1s^4$, $2s^4$. 2p as the ground state. If the restriction on the number of non-ground state orbitals is less than 4 the true ground state configuration is not even included.

These problems restricted calculations almost to a minimal basis set. (A minimal basis set contains only one wave function for each electron pair.) Adding basis elements required a limit on the number of configurations by freezing the core or restricting the number of non-ground state orbitals. These options often degraded results more than the added orbitals improved them.

15

IV. Theory

4.1 Ne_2^{+2} Binding

Excited dimer ions are expected to form in mixtures of multiply charged noble gas ions and neutral atoms due to induced polarization interactions. This polarization produces an attractive force.

$$F(r) = \frac{\alpha e^2}{\pi^2 \epsilon_o^2 r^5}$$

which is a function of the polarizability, α, and the distance between the atoms, r. (See Appendix C for the derivation of this formula.) At small separations electron and nuclear repulsions overcome the attractive force. Because of these effects a potential well in the interaction of rare gas atoms and their ions is expected. Collisional relaxation should result in a population of bound dimer molecules.

The Coulomb repulsion interaction of two positive ions leads one to believe that a bound molecular state may not exist if part of the charge shifts to the neutral atom. The energy required to ionize two rare gas atoms is less than that needed to ionize a single atom twice, requiring the charge transfer from bound Rg_2^{+2} to $2Rg^+$ to be exothermic.

Radiative charge transfer releases this energy in the form of electromagnetic radiation. In the case of interest here the reaction looks like this:

$$Ne^{+2} + Ne \rightarrow Ne^+ + Ne^+ + h\nu$$
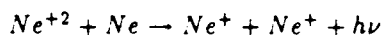
Ne has an ionization energy of 21.6 eV for the first electron and 41.0 eV for the second. This limits the radiation energy, $h\nu$, to less than or equal to 19.4 eV, which corresponds to 1.58×10^5 cm^{-1} or 63.3 nm. This lies in the vacuum ultra-violet region. The exact energy of the radiation will depend on the nuclear separation when the decay occurs, which, in turn, depends on the vibration-rotation energy level distribution.

16

Table 3. Molecular States Determined From Separated Atom: Numbers in parenthesis indicate that that term represents more than one state.

Upper Level:	
Atomic States	Molecular States
$^1S + ^3P$	$^3\Sigma_g^-, ^3\Sigma_u^-, ^3\Pi_g, ^3\Pi_u$
$^1S + ^1D$	$^1\Sigma_g^+, ^1\Sigma_u^+, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g, ^1\Delta_u$
$^1S + ^1S$	$^1\Sigma_g^+$

Lower Level:	
Atomic States	Molecular States
$^2P + ^2P$	$^1\Sigma_g^+(2), ^1\Sigma_u^-, ^1\Pi_g, ^1\Pi_u, ^1\Delta_g$ $^3\Sigma_g^-, ^3\Sigma_u^+(2), ^3\Pi_g, ^3\Pi_u, ^3\Delta_u$

A dissociative lower state is an attractive characteristic of excimer lasers since it serves to maintain the population inversion.

4.2 Ne_2^{+2} States

Herzberg's separated atom method[13] determines the possible states of the Ne_2^{+2} upper and lower levels. In this case it's actually applied to the separated atom and ions, Ne, Ne^+, and Ne^{+2}.

The atomic states and their possible molecular terms are displayed in Table 3. The upper level terms are determined from Herzberg's table for the combination of unlike atoms, since this state dissociates into Ne and Ne^{+2}. The lower level dissociates into two Ne^+ ions so its states are determined by the like atom table. Since the molecule is homonuclear in both cases all terms are either g or u symmetry, which differs from Herzberg's unlike atom case. Both g and u symmetries exist for each upper level case term specified in the table.

Ne has a ^1S ground state, but Ne^{+2} may be either ^3P, ^1D or ^1S. Hund's rules predict that the ^3P state has lower energy, and will usually be the most populated. Grotrain diagram data reveals the ^1D state to be 0.1177 a.u. (3.204 eV) above the ^3P, and the ^1S state 0.2540 a.u. (6.887 eV) above. The focus here is primarily on the states with multiplicity 3 that result from combining the ^1S Ne and ^3P Ne^{+2} ground states into a diatomic molecule. However, all states are considered

17

Table 4. Selection Rules for Ne_2^{+2}

$\Sigma \leftrightarrow \Sigma$	$\Sigma \leftrightarrow \Pi$	$\Pi \leftrightarrow \Pi$
$\Pi \leftrightarrow \Delta$	$\Sigma \nleftrightarrow \Delta$	
$3 \leftrightarrow 3$	$1 \leftrightarrow 1$	$1 \nleftrightarrow 3$
$g \leftrightarrow u$	$g \nleftrightarrow g$	$u \nleftrightarrow u$
$- \leftrightarrow -$	$+ \leftrightarrow +$	$- \nleftrightarrow +$
($\leftrightarrow$ indicates allowed transitions and $\nleftrightarrow$ are forbidden)		

Table 5. Allowed Triplet Transitions

$^3\Sigma_u^- \rightarrow\ ^3\Sigma_g^-$	$^3\Pi_u \rightarrow\ ^3\Pi_g$
$^3\Sigma_u^- \rightarrow\ ^3\Pi_g$	$^3\Pi_g \rightarrow\ ^3\Sigma_u +$
$^3\Sigma_g^- \rightarrow\ ^3\Pi_u$	$^3\Pi_g \rightarrow\ ^3\Pi_u$
$^3\Pi_u \rightarrow\ ^3\Sigma_g^-$	$^3\Pi_g \rightarrow\ ^3\Delta_u$

The lower level could form in many states, both singlet and triplet, but states that the upper level will transition to are most critical.

4.3 Radiative Transitions

The probability of making a transition from state A to state B with emission of a photon is proportional to the transition moment $< A|ex|B >$. Selection rules result from the fact that this integral can vanish based on the symmetry properties of the A and B orbitals. For homonuclear diatomic molecules such as Ne_2^{+2} the selection rules in Table 4 limit the non-zero transition moments from the triplet $Ne^{+2} + Ne$ states of Ne_2^{+2}. This restricts triplet transitions to those shown in Table 5.

V. Results and Discussion

5.1 Helium Test Case

The final 62 element basis set containing large and small exponents produced the most variationally superior results for the He atom and the He_2^{+2} dimer. Spacing between the first seven excited states of the atom matched spectroscopic values within 1 or 2 mH (mili-Hartrees). They were all shifted up by 5 or 6 mH from the exact energy values, as shown in figure 1.

Figures 2 through 5 show Diatom results from the 62 element basis and make comparisons with Gaussian 86 and Cohen and Bardsley's[1] data. At the ground state local minimum near R = 1.3 a.u. Diatom's energy is 24 mH below the Gaussian 86 value. Diatom's ground state data are practically identical to Cohen and Bardsley's, and the excited state values are never more than 2 mH apart between 1 and 8 a.u. nuclear separation.

These results and Cohen and Bardsley's both predict a potential well of 15 mH in the Σ_u state and 11 mH in the Σ_g state for the upper level of He_2^{+2} correlating to He^{+2} and He.

5.2 Atomic Calculations: Ne, Ne$^+$, Ne^{+2}

In the separated limit the Ne_2^{+2} dimer dissociates into either two Ne^+ ions, or one Ne atom and one Ne^{+2} ion, so the basis set should be able to reasonably represent the ground state of each atomic species.

Atomic energies for various optimized basis sets are shown in Appendix A. The 3s exponents in Appendix A optimized an electronic energy with one 2p orbital excited to the 3s level. Both ground state and the electronic excitation energies are shown for each Diatom basis. The first basis set shown under Diatom results in Table A-2 of Appendix A was used for Ne_2^{+2} computations. Energies computed from this basis are -127.707, -127.353, and -126.008 a.u. for Ne, Ne^+, and Ne^{+2} respectively, compared to exact values of -129.047, -128.025, and -126.749 a.u.

Table 6. Comparison of Ionization Energies

	Ne$^+$ Basis	Reoptimized	Grein	Experiment
Ne$^+$	18.76	20.31	21.34	21.56
Ne^{+2}	59.81	60.68	61.52	62.63

As discussed in the Basis Set Optimization section double zeta basis sets produced variationally superior atomic energies, but they were too large for dimer calculations. The error in the atomic energies above may seem significant, but is actually only 1%. Dimer energies were shifted up by a similar amount. but general characteristics of energy surfaces should still be reliable.

Another measure of a basis set's usefulness is the ionization energies it calculates. Table 6 compares calculated ionization energies, in eV, from the 1s, 2s, 2p, 3s, 2p' basis in Appendix A to recent calculations in the literature and experiment.[6] The Ne$^+$ Basis column gives the differences in total electronic energy of Ne, Ne$^+$, and Ne^{+2}, all calculated from the same basis with exponents optimizing the Ne$^+$ ground state. The total energies used to produce the Reoptimized column were computed with basis sets whose exponents had been individually optimized for the respective atomic ground states. The third and fourth columns were taken from Grein's paper where he reported results of CI calculations which used Gaussian basis orbitals.

5.3 Ne$_2^{+2}$ Potential Energy Surfaces

Figures 6 through 13 are plots of Diatom calculations on the Neon dimer dication. For this 18 electron system the basis set consisted of 12 wave functions. 6 for each nucleus, with the four 1s core electrons frozen. Most states required configurations to be restricted to having only two orbitals differ from ground state in the CI expansion. The exponents of this basis, which are shown in the first entry of Table A-2, Appendix A, were optimized for the Ne$^+$ ion. For comparison. the Helium test case used 62 functions to model 2 electron orbitals, with no frozen orbitals and no restrictions on the number of non-ground state orbitals.

Figures 6, 7 and 8 illustrate the energy surfaces of triplet states, which are the primary states of interest here. Figure 8 has plus marks at each data point calculated. Energies were computed at the same nuclear separations for each state. The number of non-ground state orbitals was limited to two for the $^3\Sigma$ and $^3\Pi$ states, while the $^3\Delta$ calculation required no restriction.

Figure 9 shows the potential wells of the $^3\Sigma$ states, which both have a depth of 30 mH, along with the Π g and u states having well depths of 17 and 29 mH respectively. The $^3\Sigma$ well supports more than 21 bound vibrational modes.[19]

Figure 10 indicates that the upper level of the singlet Σ state may be dissociative. This computation limited the number of non-ground state orbitals to 3. Figures 11 and 12 show $^1\Pi$ and $^1\Delta$ energies from a computation allowing up to 4 non-ground state orbitals in the CI expansion.

Figure 13 shows the singlet upper levels. The peak in the $^1\Delta$ upper level is unusually sharp. This may be due to a curve crossing between the dimer state corresponding to Ne and Ne^{+2} (1s^2, 2s^2, 2p^4) and the next electronic level corresponding to Ne and Ne^{+2} (1s^2, 2s, 2p^5). A similar peak, not quite as pronounced, exists in the $^1\Sigma$ and $^1\Pi$ data.

Diatom computed two $^3\Sigma_u^+$ states and one $^3\Sigma_g^-$ state at the lower level just as the tables in Herzberg predict.[13] Also, Diatom gave $^3\Sigma_u^-$ and $^3\Sigma_g^-$ states at the upper level as expected. The code did not indicate whether the g states were Σ_g^+ or Σ_g^- symmetry, but Herzberg indicates that they are both Σ_g^-.

The electronic energy levels shown can be verified by examining their values at large nuclear separation, R, where they are approaching the dissociated limit. The $^3\Sigma$ ground state reaches an energy of -254.655 a.u. at R = 20, and the fist excited state gets down to -253.801 a.u. Adding up the computed ground state energies of the dissociated atomic and ionic species these values at large R should be near -254.706 and -253.715 a.u.

It is interesting to note that Diatom computed an energy for the Dimer at large separations which was less than the sum of the corresponding atomic species' energies which it also calculated.

One would expect the large separation value to approach the sum of the atomic values, or a value slightly higher. The lower level behaved this way, but the upper level went below what was expected to be it's lower limit. This anomaly remains unexplained at this point.

The next measure of the calculation's accuracy considered was the difference between energy levels at large separations. At R = 20 the $^3\Sigma$ difference is 0.854 a.u. compared to the true value of 0.712. This discrepancy is expected. Since the basis set is optimized for Ne^+ it should model the lower level at large R much better than the upper level, increasing the difference between the two. Expanding the basis to include double zeta ground state orbitals should drastically reduce this discrepancy.

The above analysis can be applied to data for all states with similar results. Lower level plots were all the same within a few mH. At large nuclear separations every state approached -254.654 $\pm$ 0.0015 a.u. Upper level plots vary in shape, but all approach a limit at large R between -253.77 and -253.81, well below the limit of -253.715 predicted by atomic calculations.

The first difficulty apparent with the results was the fact that the excited state decreased at large R when it is expected to increase. Figure 6 contains a local minimum near R = 4.5 a.u. of energy -253.759 a.u. This is the lowest excited state energy computed for all points except the last one at R = 20. The local maximum at R = 7 is -253.729 a.u.

The fact that the curve is so level over such a large range and knowing that the results are not precise prevent detailed predictions of the true shape of the upper level. Up to R = 7 a.u. the energy surface appears to reach the expected minimum increasing toward the expected limit at large R of -253.715 a.u. Diatom's computation of lower energies than expected for large R is a puzzling anomaly. With this in mind, the data indicates there probably is a minimum in the curve somewhere above 3.0 a.u.,but the maximum at R = 7 may or may not exist in the true Ne_2^{+2} energy surface. Below R = 3 all curves turn sharply upward.

The $^3\Pi_u$ and $^3\Pi_g$, singlet $^1\Pi_u$, and $^1\Delta_u$ and $^1\Delta_g$ curves all contain a local minimum near the

22

same point as the $^3\Sigma$. (see Figures 9 and 13) which further supports the idea that a bound state may exist in the upper level of the Ne_2^{+2} curve due to induced dipole attraction.

At R = 4 a.u., where the upper level computed minimum is found, the energy difference between the $^3\Sigma_g^-$ lower state and the $^3\Sigma_u^-$ upper state is 0.705 a.u. (19.2 eV.) A transition here would have a wavelength of 64.6 nm. The lower level energy at R = 3 a.u. is considerably higher so that a transition there would radiate 0.647 a.u. (17.6 eV) of energy at 70.4 nm wavelength. The exact wavelength emitted is dependent on the location of the minimum, and will vary further for different vibrational modes. The actual wavelength will be somewhere near the range above, perhaps at a longer value since the upper curve is expected to decrease more than the lower curve with improved basis sets.

One more key result is that the surfaces do not cross at an energy low enough to allow non-radiative charge transfer transitions, except in high energy collisions. At the shortest internuclear distance computed, R = 0.9 a.u., the separation between states was still over 0.2 a.u. (5.4 eV), and the upper level energy was more than 15 a.u. (407 eV) above its value at large R.

VI. Recommendations

The Diatom code has tremendous capabilities, as illustrated by the Helium test case. If the problems presented in the previous section were fixed the energy surfaces could quickly be accurately calculated. Transition moments could also be found for He_2^{+2} to compare to Cohen and Bardsley's data[1] and then Ne_2^{+2} transition moments could also be computed. After obtaining a more accurate potential energy curve one could calculate the vibrational modes of the dimer.

This research could continue by working with Harvey Michels to improve Diatom's performance. The present version could be run with a full double zeta basis set on a CRAY computer allowing for more configurations. With some of the code's deficiencies corrected and greater computational capabilities, this approach can be extended to other rare gasses including heteronuclear cases.

As a supplement to further computer calculations, a Fourier Transform Mass Spectrometry experiment could be conducted to look for the presence of the Ne_2^{+2} over a range of pressures to study what conditions it forms under, and what quantities it can be found in.

VII. Conclusions

With the results of this research several conclusions can be drawn. First, nonradiative charge transfer is not likely to occur since such a transfer would require a collision with hundreds of eV energy. The energy level of any possible curve crossings is prohibitively high. The minimum in the excited state is at a large enough nuclear separation that tunneling should not be a problem either, however further study on that phenomenon may be warranted. These results indicate that a minimum in the upper level does exist which may be populated through three body collisions. Finally, the lower level is clearly dissociative as expected.

Energy Levels of the Helium Atom: Top lines are Diatom results
bottom lines are from Grotrain Diagram
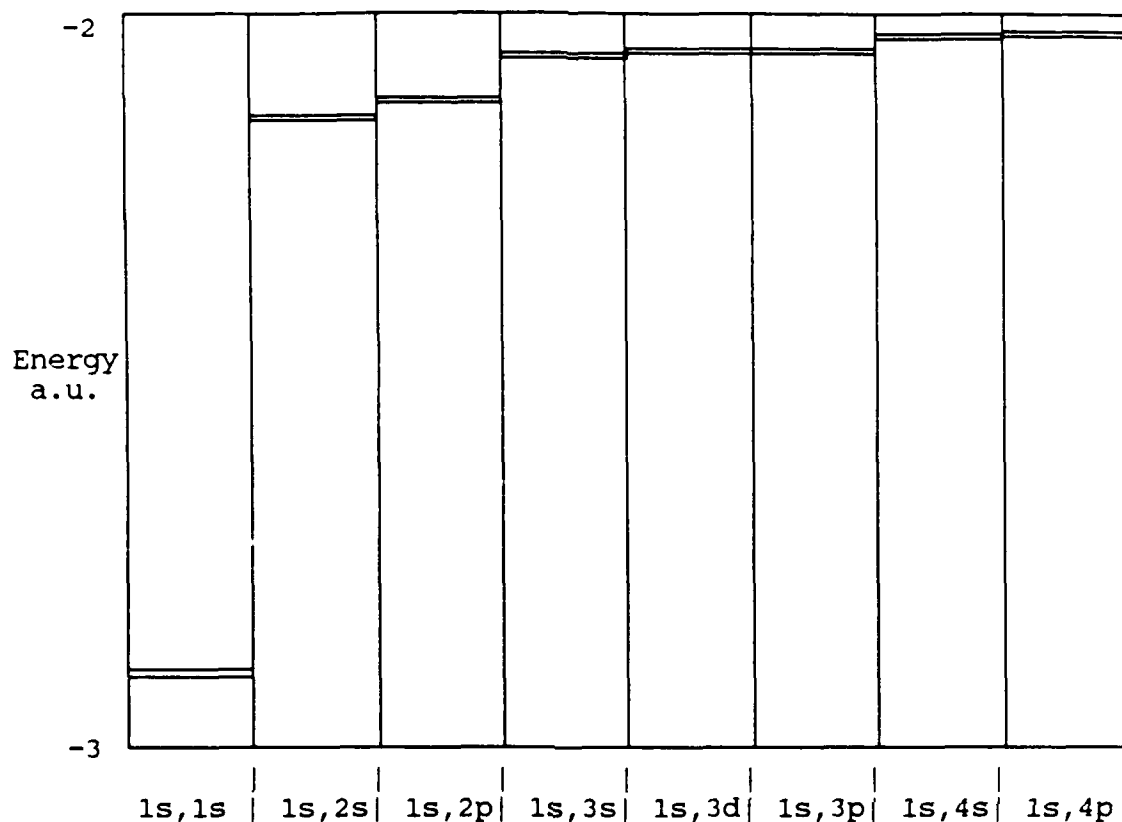
Difference Between Diatom Energies and Exact Energies
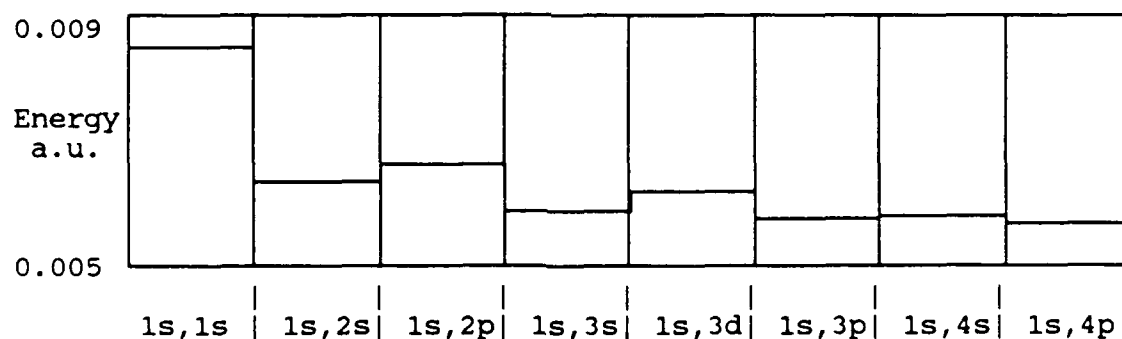
Figure 1.   Atomic Energy Levels of the Helium Atom: The top chart above shows the first eight
energy levels of the Helium atom, both exact values and as calculated by Diatom. The
bottom chart shows the difference between the two for the same electronic energy levels.
If the energies were shifted down by 6 mH the excited states would all be within a mH
of the exact values

26

He2++ ground state and first excited state from a 62
element basis set on diatom, full CI.
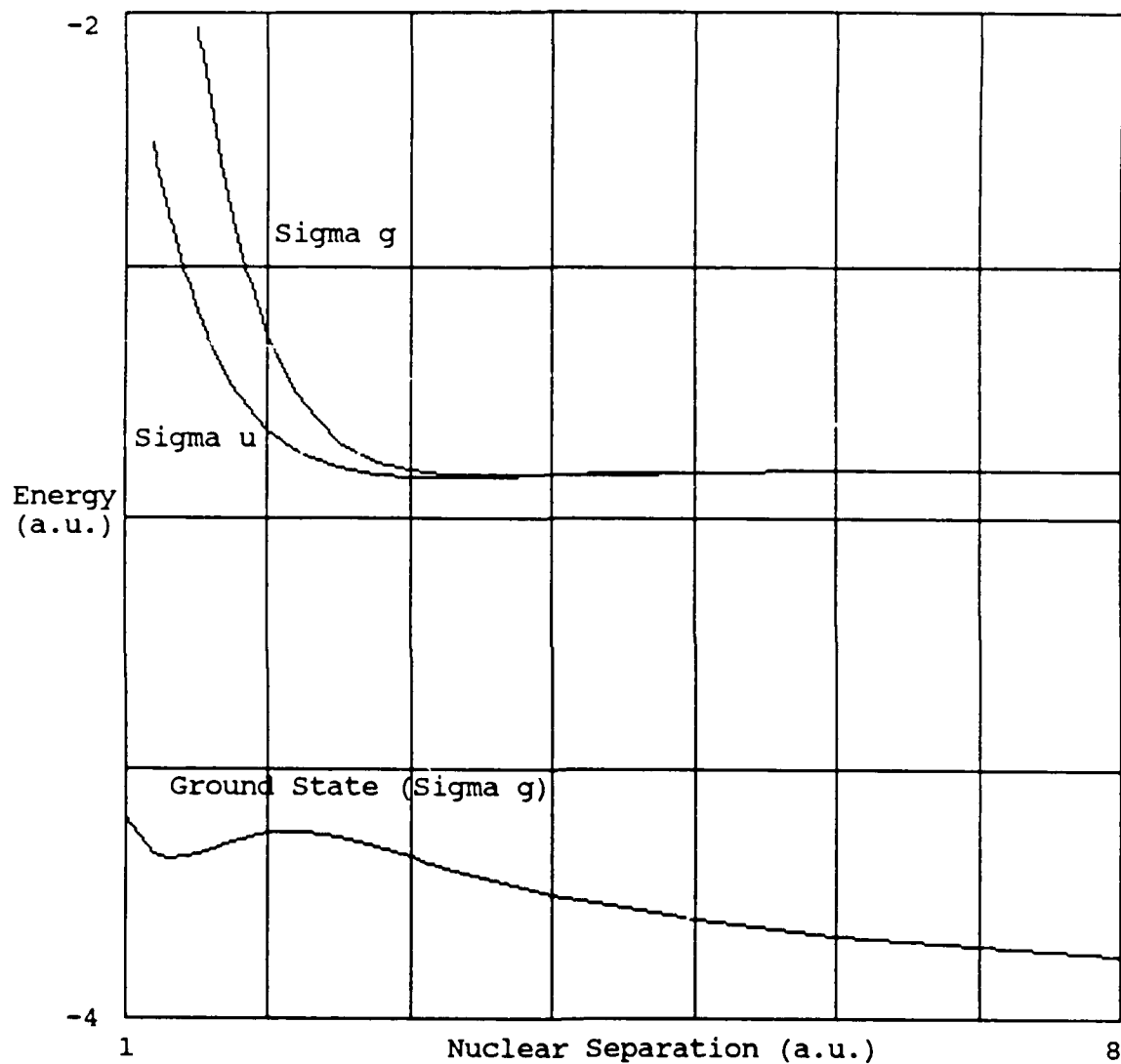
Figure 2. Diatom Results: The plots above are the energies of the Helium dimer dication ground
state, which is a Σ_g state, and the energies of the first electronic excitation for both Σ_g
and Σ_u states. This basis set used a single 1s function for the ground state, but had
two of each excited state orbitals, one optimized for the level of excitation it represents,
and the other optimized to minimize the ground state. All states are singlet states.

27

He2++ Ground State Potential Energy
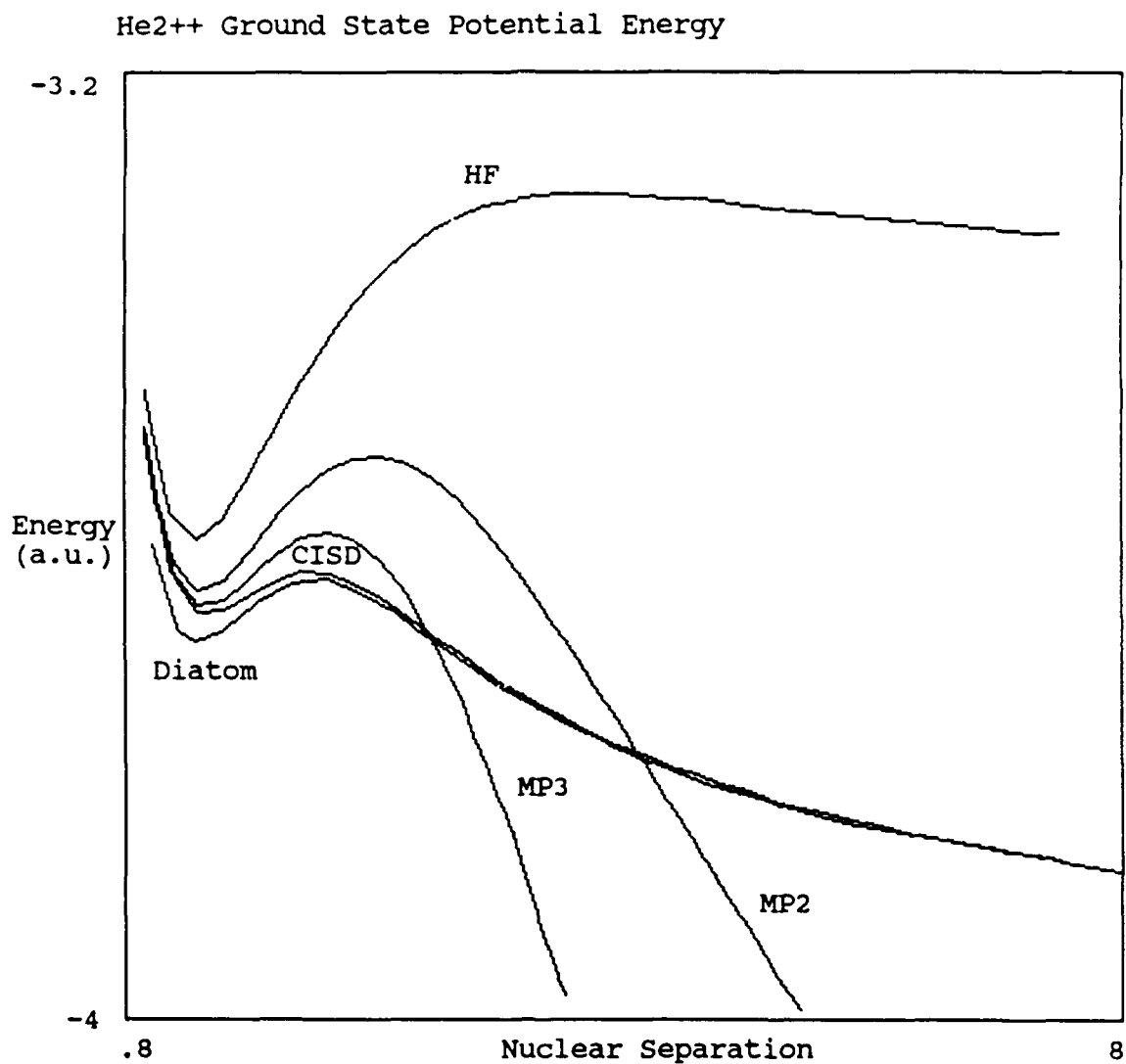
Figure 3. Comparison of Various Gaussian-86 6-31G** Results to Diatom's Best: The HF curve
is a Hartree Fock calculation. MP2 and MP3 results are nonvariational perturbation
results. The CISD curve used the single and double excitation option of Gaussian-86,
which is full CI in this case. Diatom clearly has the lowest energy at short nuclear
separations, and is slightly lower than Gaussian-86 CI at larger distances also.

Diatom and Cohen and Bardsley's Ground States From 1 to 3 a.u. Separation
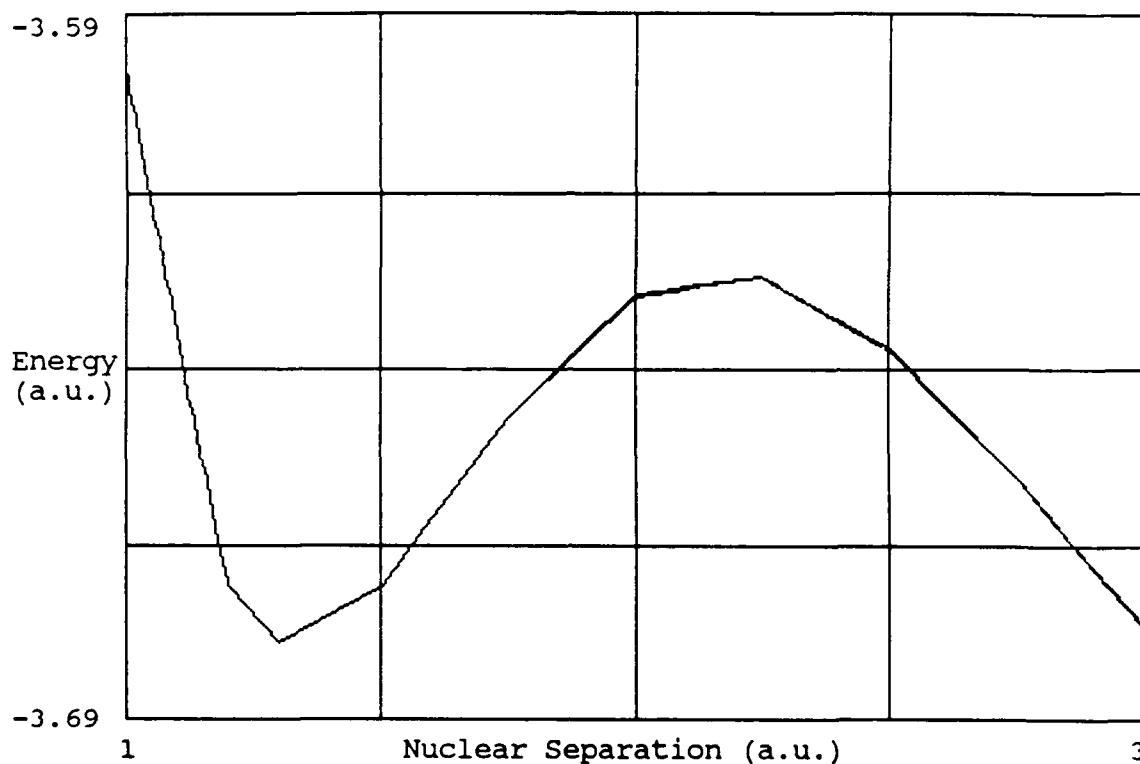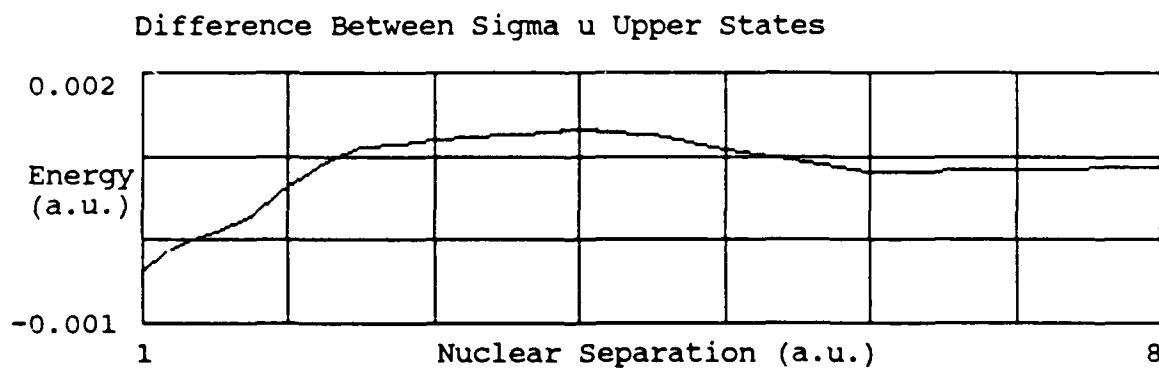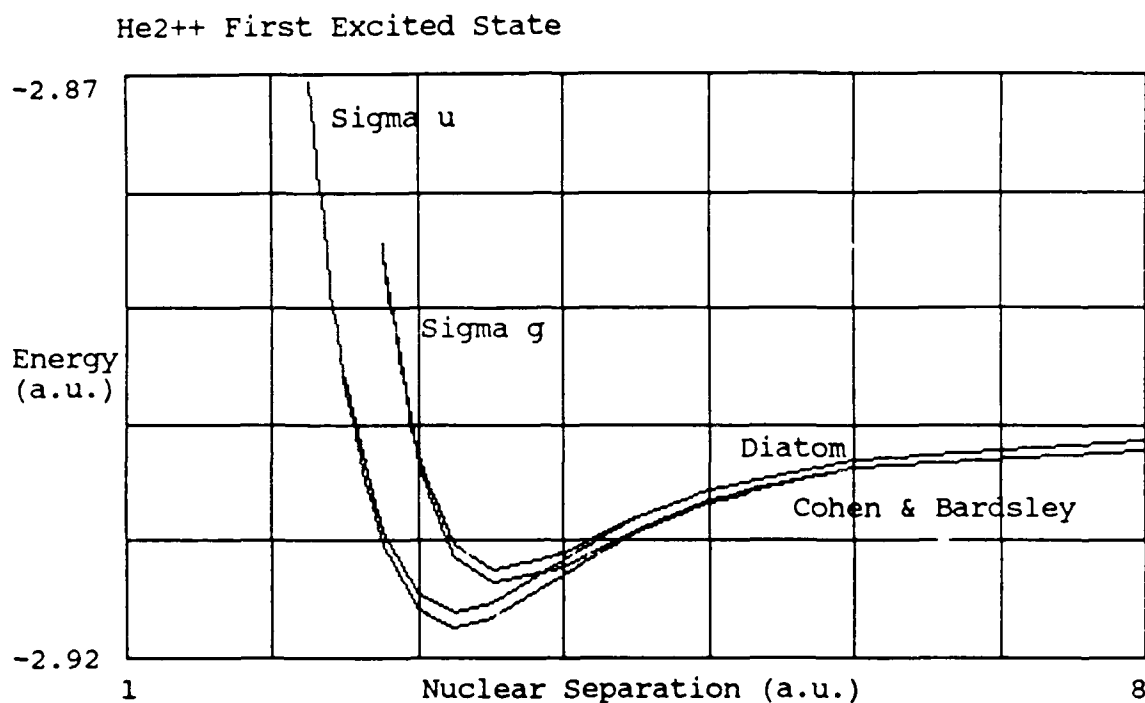

Difference Between Two Cases From 1 to 8 a.u. Separation
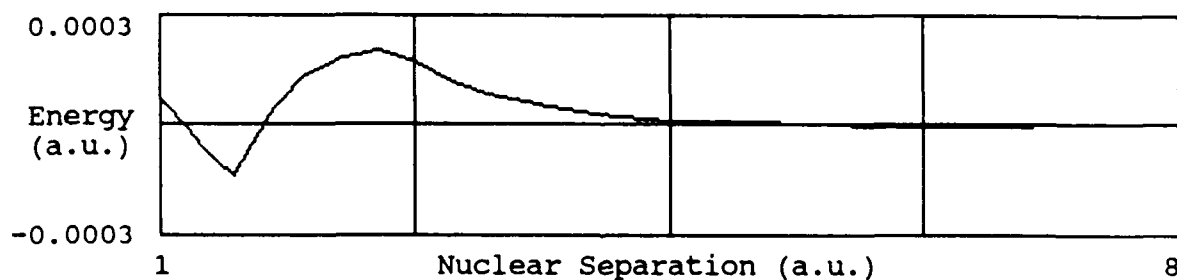
Figure 4. Diatom Ground State Comparison to Cohen and Bardsley's Results: The top plot shows the energies of the Helium dimer dication ground state, which is a Σ_g state. It may appear that there is only one plot because the two are so close. Only a small portion of the curve is shown, magnified to the point that individual data points are easily distinguishable. The lower curve is the difference between the two, less than 0.3 mH (miliHartree) at all points.

He2++ First Excited State

Difference Between Sigma u Upper States

Figure 5. Diatom First Excited State Comparison to Cohen and Bardsley's Results: The top plot shows the energies of the Helium dimer dication, Σ_g and Σ_u states. Ageement is not as close with the ground state, but is still within 1.5 mH as shown in the lower curve.

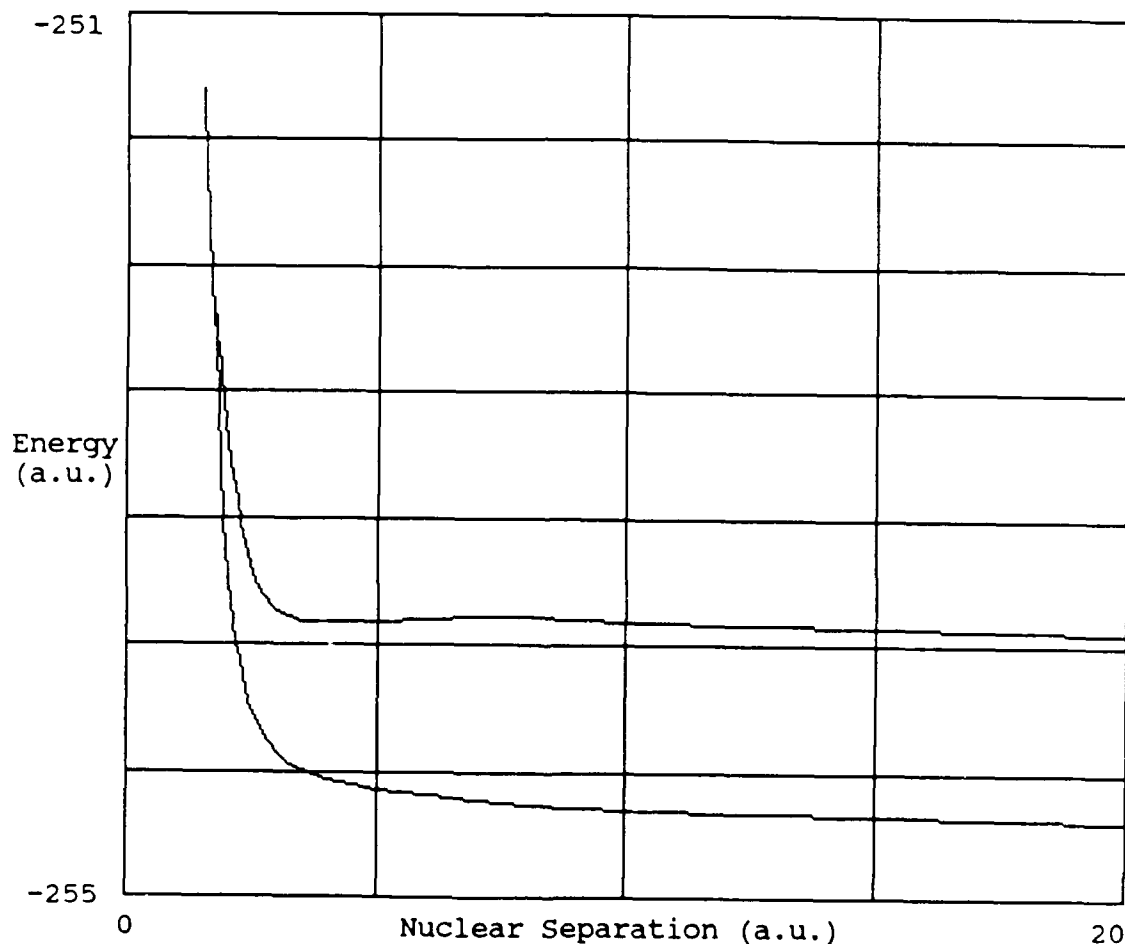Ne2++ Triplet Sigma State Energies Using 12 Element Basis

Figure 6. Neon Dimer Dication $^3\Sigma$ Energies: This plot shows two $^3\Sigma$ energy surfaces. The lower level has u^+ symmetry and dissociates to two Ne^+ ions. The upper level is Σ_u^- and dissociates to a Ne atom and Ne^{+2} ion. Diatom also computed a Σ_g^- and a second Σ_u^+ state for the lower level, along with Σ_g^- for the upper level as predicted by the Hertzberg tables. These are not shown because they are indistinguishable on a plot of this scale. This calculation used a 12 element basis set with single functions for each orbital. 1s through 3s.
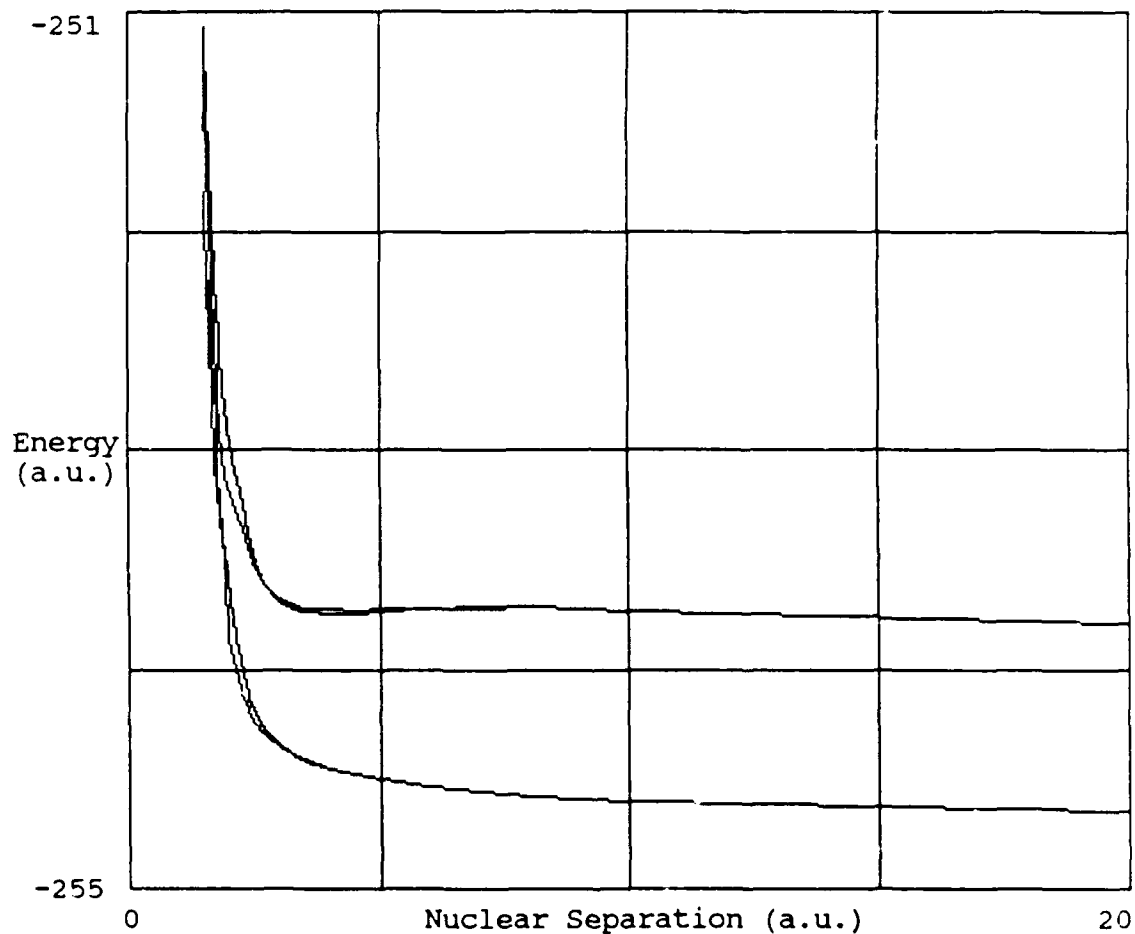
31

Figure 7. Neon Dimer Dication ³Π State Energies: This plot shows the ³Π lower and upper level energies computed by Diatom using a 12 element basis set with single functions for each orbital, 1s through 3s. Each level has a state with g symmetry and a state with u symmetry.

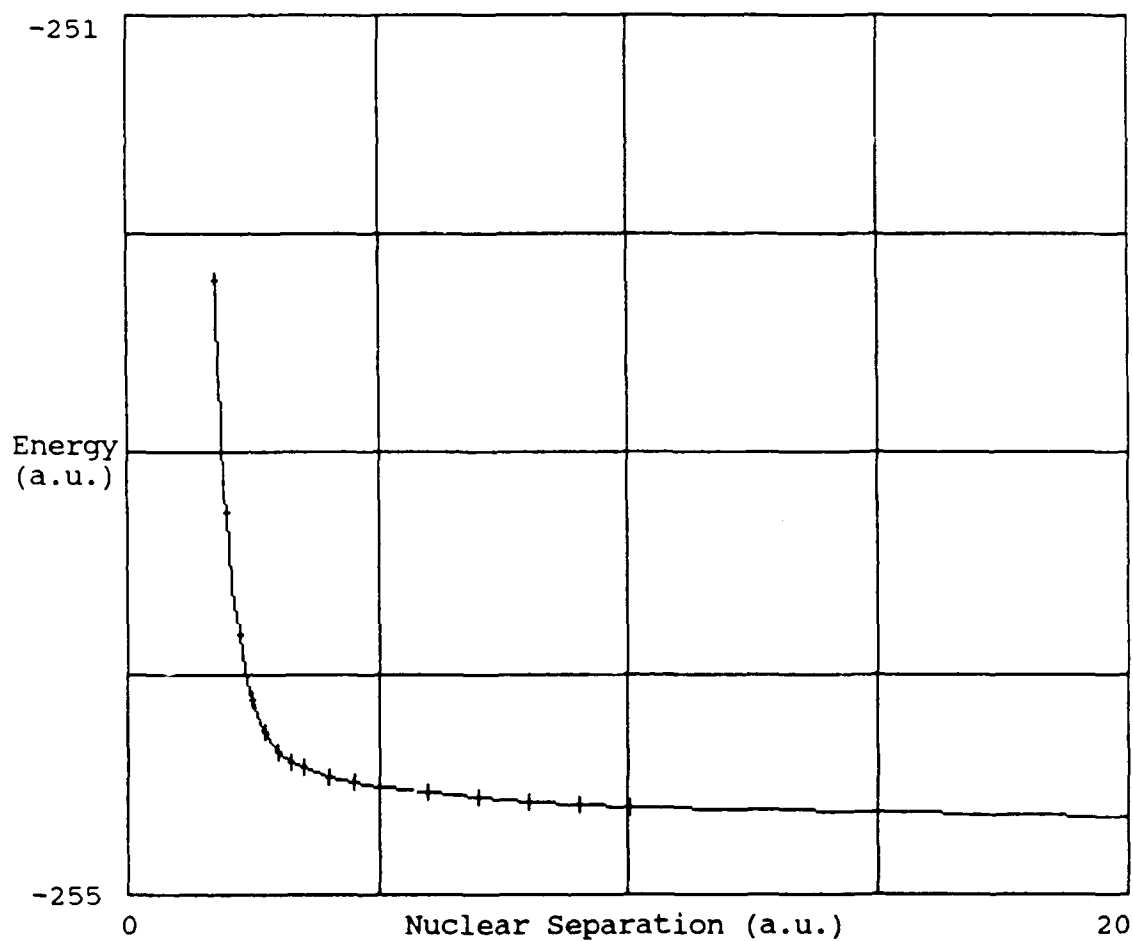## Ne2++ Triplet Delta State Energies Using 12 Element Basis

Figure 8.   Neon Dimer Dication $^3\Delta$ Energies: This plot shows the $^3\Delta$ energy surface which is a lower level surface dissociating to two Ne^+ ions. Plus marks show the location of data points. This calculation used a 12 element basis set with single functions for each orital, 1s through 3s.

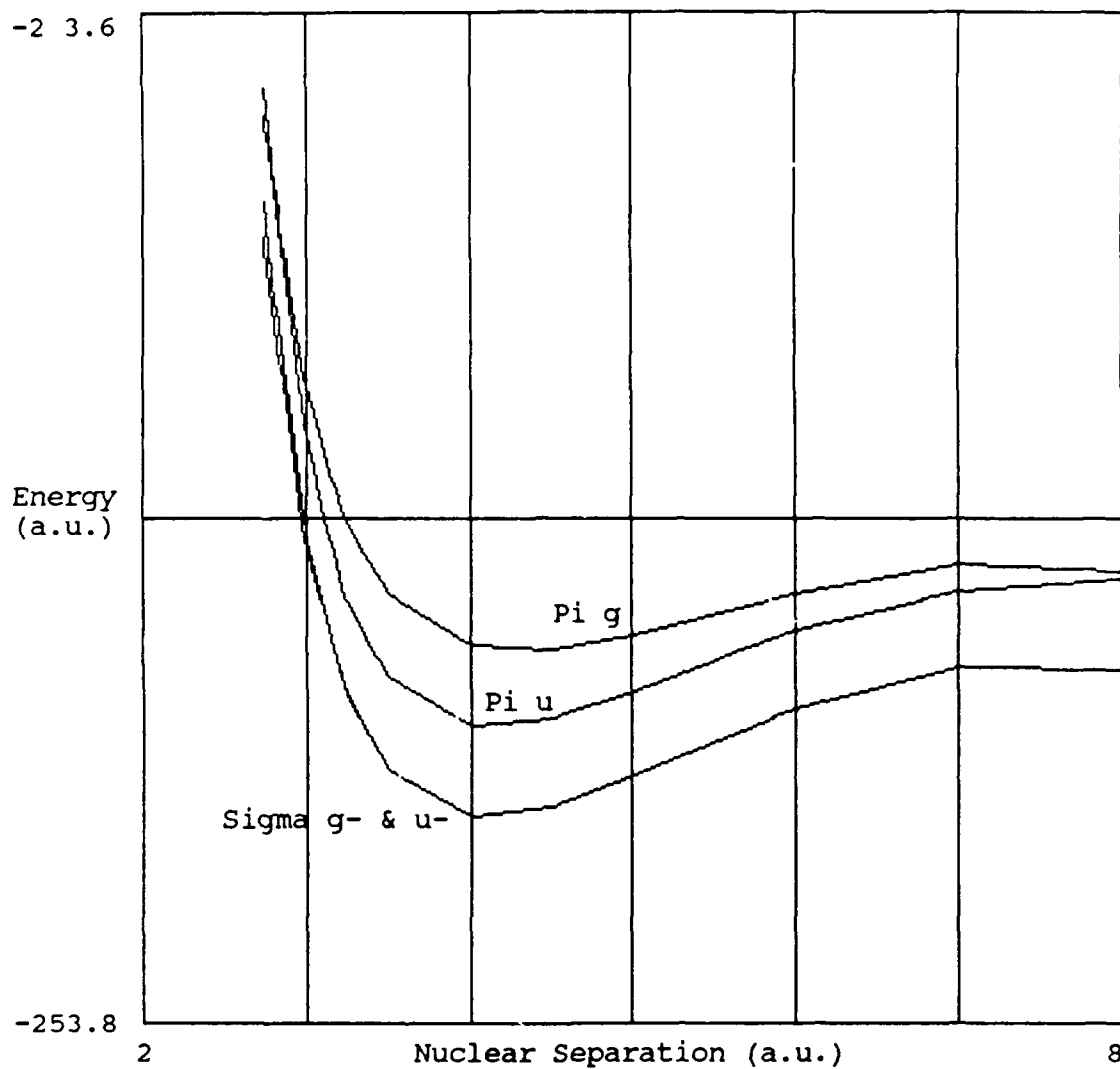## Ne2++ Triplet Sigma and Pi Upper Levels

Figure 9. Neon Dimer Dication $^3\Sigma$ and $^3\Pi$ Upper Levels: This plot of the $^3\Sigma$ and $^3\Pi$ upper level energies for nuclear separations, R, from 2 to 8 a.u. computed by Diatom with the 12 element basis, 1s, 2s, 2p, 3s. The Σ_u^- state has a slightly lower energy than the Σ_g^- state. Note the energy minimum near R = 4.

34

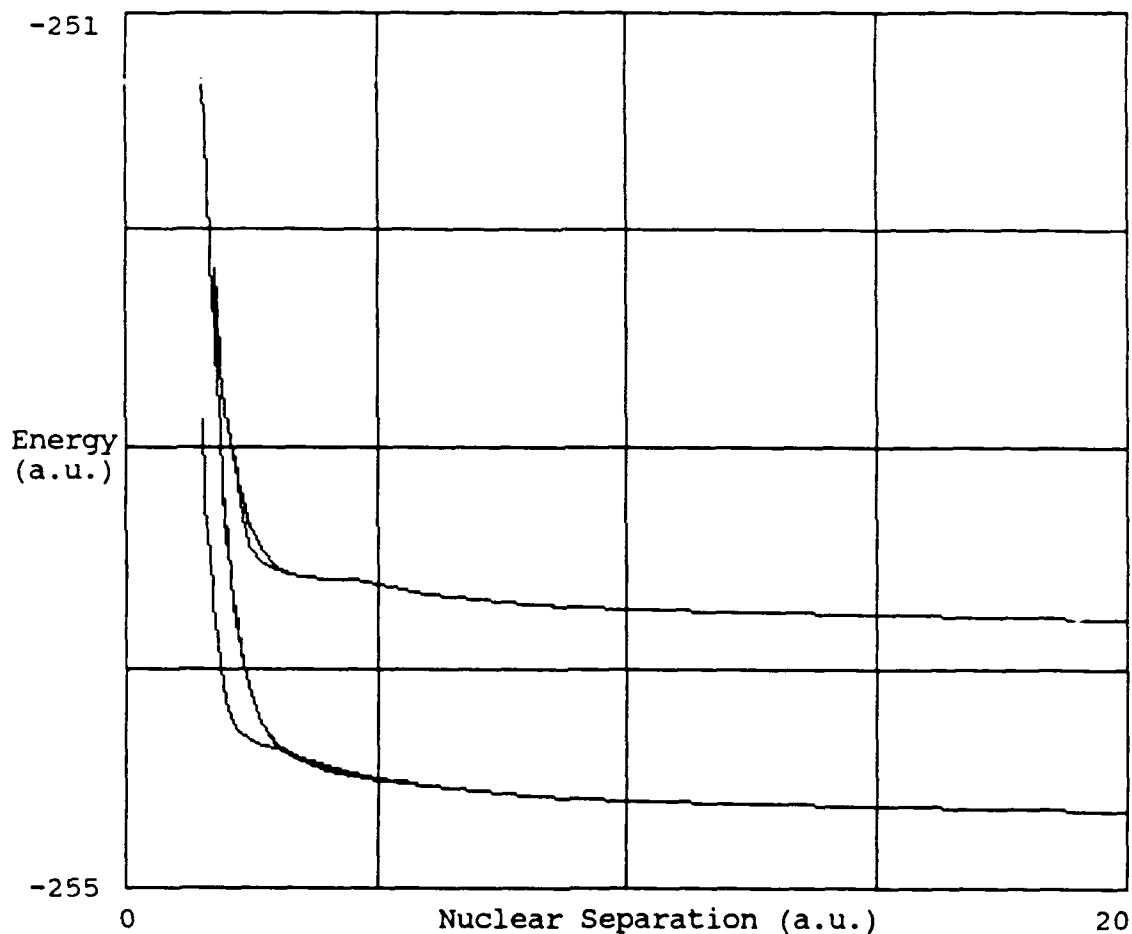## Ne2++ Singlet Sigma State Energies Using 12 Element Basis

Figure 10. Neon Dimer Dication $^1\Sigma$ Energies: This plot shows the $^1\Sigma$ lower and upper levels computed by Diatom using a 12 element basis set with single functions for each orbital, 1s through 3s. The lower level has two Σ_g^+ ions, while the upper level has a Σ_g^+ state and a Σ_u^+ state, which both dissociate to a Ne atom and a Ne^{+2} ion. Note that there are no local minimua in these energy surfaces.

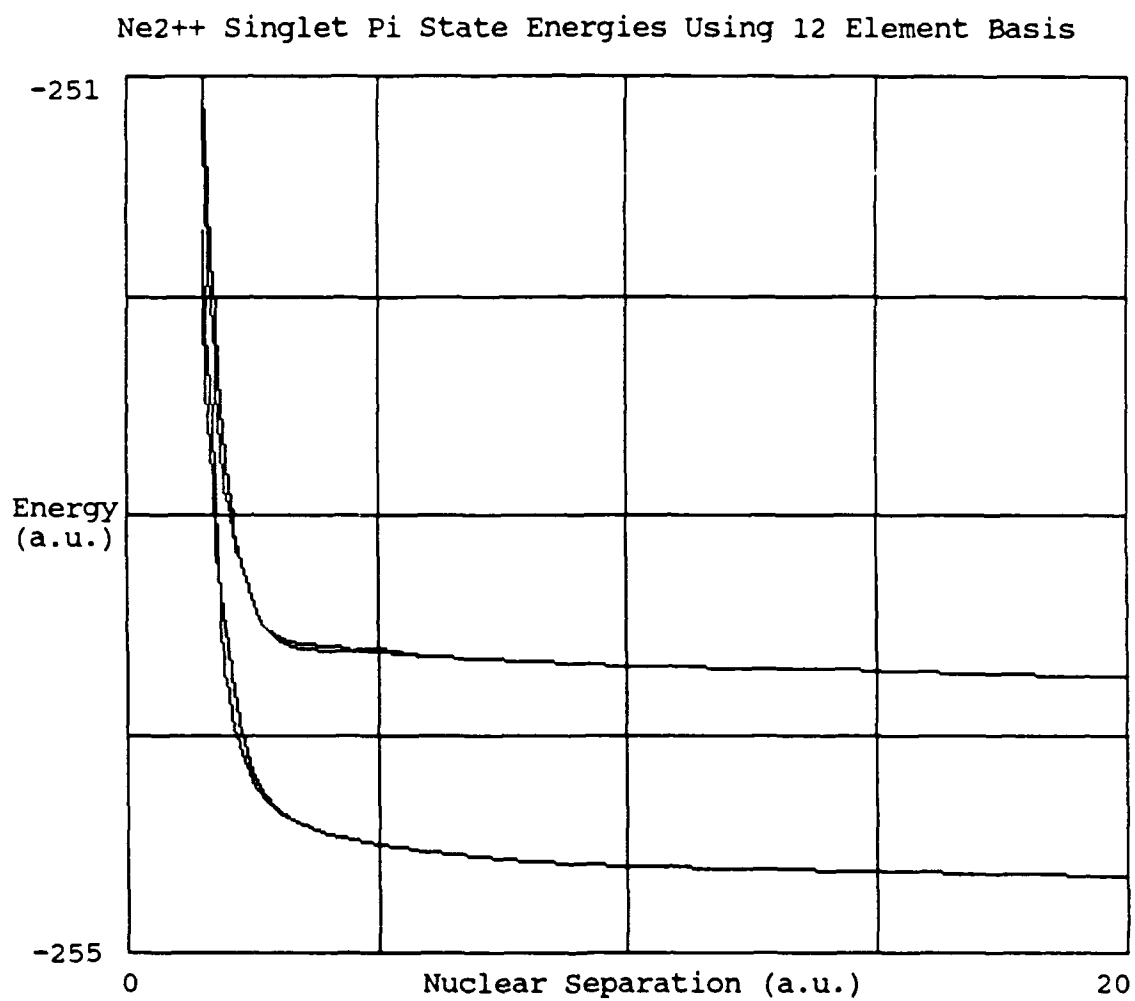**Ne2++ Singlet Pi State Energies Using 12 Element Basis**

Figure 11. Neon Dimer Dication $^1\Pi$ State Energies: This plot shows the $^1\Pi$ lower and upper level energies computed by Diatom using a 12 element basis set with single functions for each orbital, 1s through 3s. Each level has a state with g symmetry and a state with u symmetry.

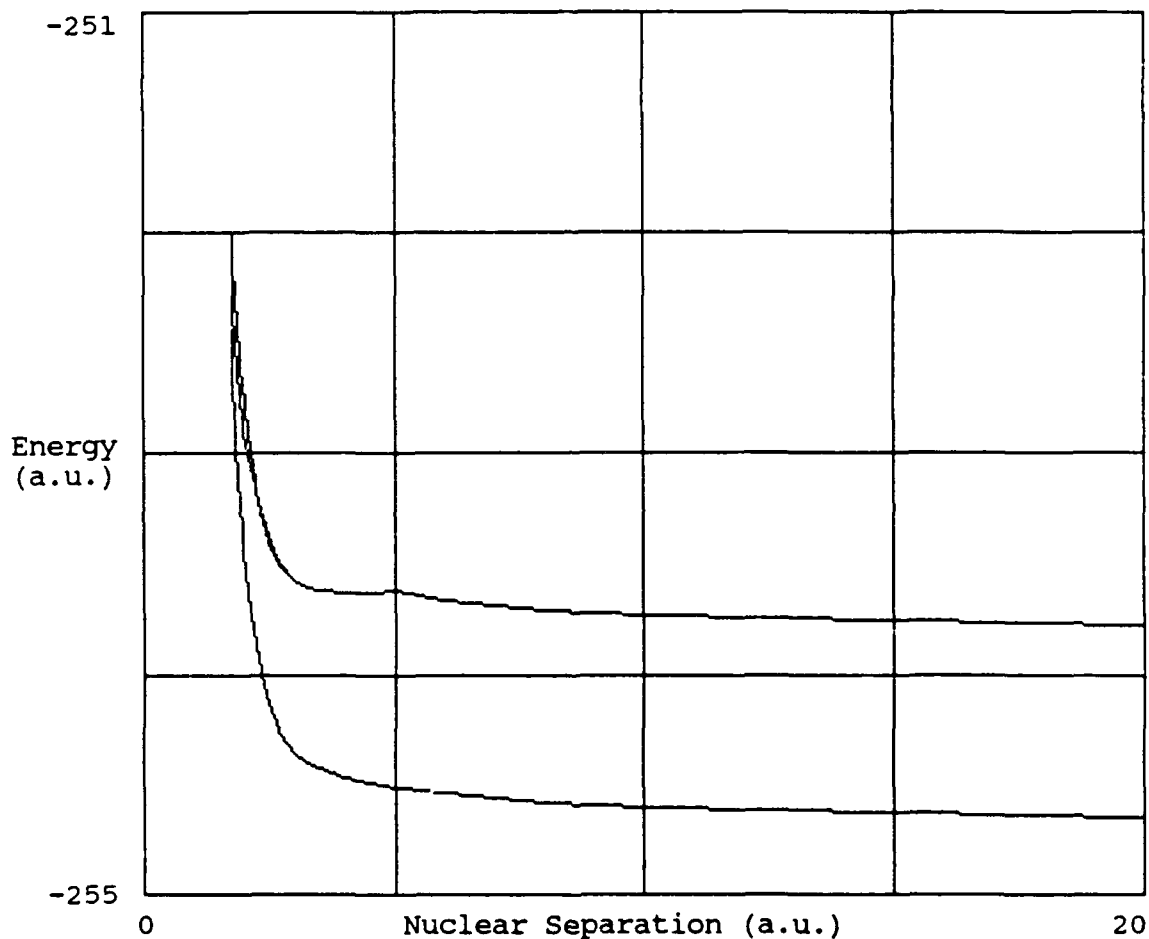## Ne2++ Singlet Delta State Energies Using 12 Element Basis

Figure 12. Neon Dimer Dication $^1\Delta$ Energies: This plot shows the $^1\Delta$ ground state and upper level states computed by Diatom using a 12 element basis set with single functions for each orbital, 1s through 3s. The ground state is a Δ_g state which dissociates to two Ne^+ ions, while the upper level has a Δ_u and a Δ_g state which dissociate to a Ne atom and a Ne^{+2} ion in their electronic ground states.
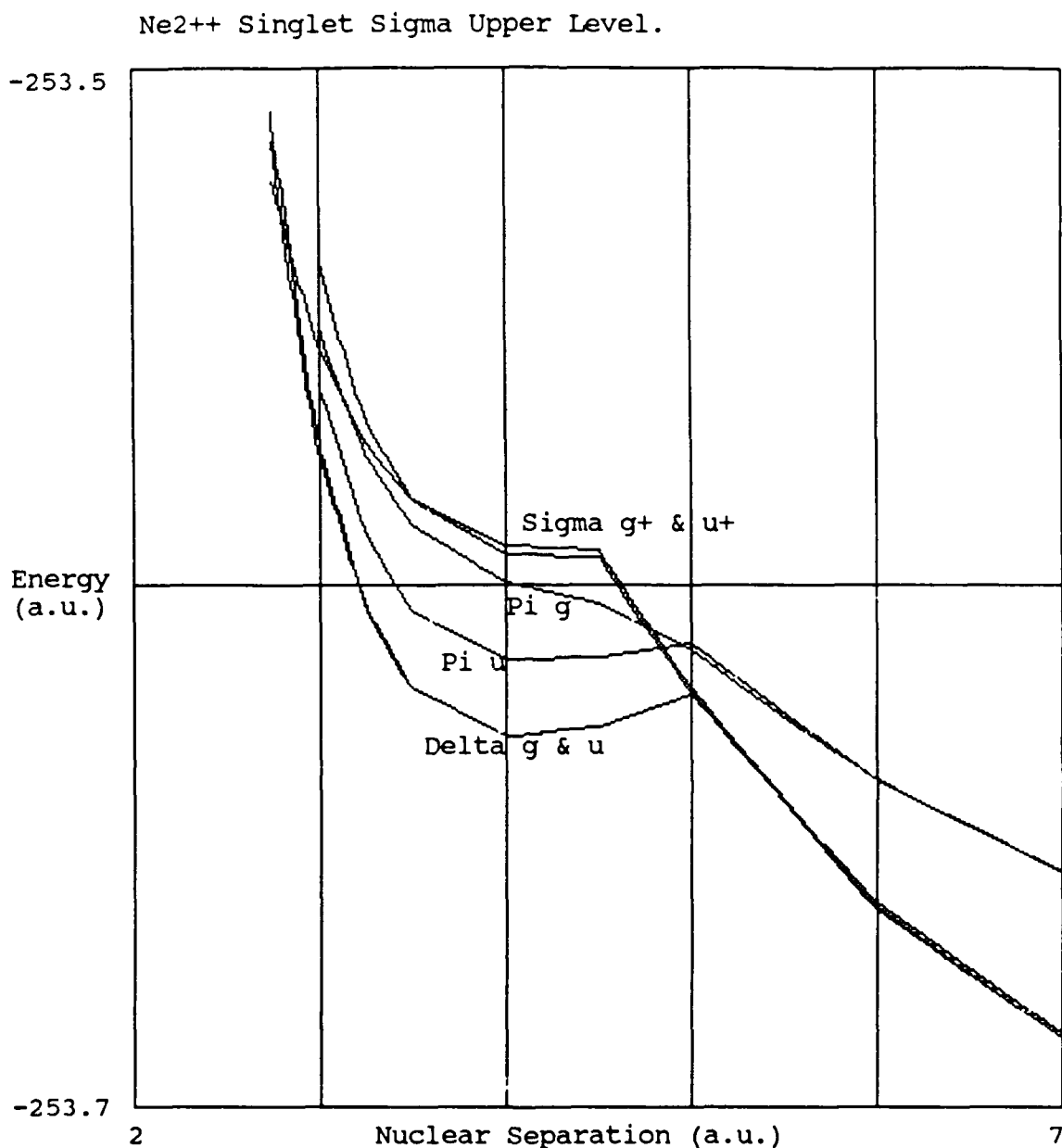
37

Ne2++ Singlet Sigma Upper Level.

Figure 13.   Neon Dimer Dication Singlet Upper Levels: This is a plot of the $^1\Sigma$, $^1\Pi$, and $^1\Delta$ upper level energies for nuclear separations from 2 to 7 a.u. computed by Diatom with 12 element basis, 1s, 2s, 2p, 3s. The Σ_u^+ curve is slightly lower than the Σ_g^+ in the neighborhood of R = 4. The Π_u energy has a minimum at R = 4, while the higher Π_g plot does not. The Δ state energy surfaces have the most pronounced minima. Though the Δ_g and Δ_u energies are almost the same, the u state is slightly lower at most nuclear separations.

Appendix A. *Atomic Calculations*

The following tables list energies for various basis sets. Note how adding primed functions improves the ground state and first excited state energies for all three Neon species considered. The affect is greater on the excited state, and the 2p orbital has the largest impact, followed by 1s and finally 2s. Adding a 3s' function may have improved the excited states even more, but this was of little consequence for this Ne_2^{+2} effort.

Diatom results are all from CI calculations. Gaussian-86 results gives energies from Hartree Foch calculations, single and double excitation CI, and CISD energies with a size consistancy correction.

Table 7. Gaussian-86 Results

BASIS SET	ATOM /ION	HARTREE FOCK GROUND STATE	CISD GROUND STATE ENERGY	CISD WITH SIZE CORRECTION
STO-3G	Ne	-126.604525		
	Ne$^+$	-126.061472		
	Ne^{+2}	-124.574003		
D95V	Ne	-128.522354	-128.620695	-128.622298
	Ne$^+$	-127.794142	-127.849733	-127.850225
	Ne^{+2}	-126.345789	-126.371806	-126.371902
6-311G**	Ne	-128.522553	-128.728396	-128.732595
	Ne$^+$	-127.796737	-127.957841	-127.960196
	Ne^{+2}	-126.350068	-126.471882	-126.473112

Table 8. Diatom Results: Exponents optimized to Ne^+

BASIS SET	ATOM /ION	GROUND STATE ENERGY	ONE 3S EXCITATION
1s=9.6353 2s=2.9770 $2p_o$=3.1091 $2p_1$=3.0668 3s=1.1230	Ne Ne^+ Ne^{+2}	-127.70717 -127.35285 -126.00796	-127.46399 -126.481957 -124.4879
1s=9.2766 2s=3.0583 $2p_o$=3.1180 $2p_1$=3.0632 $1s'$=14.9590 3s=1.1150	Ne Ne^+ Ne^{+2}	-127.75335 -127.410678 -126.078562	-127.52401 -126.55357 -124.570695
1s=9.7182 2s=3.3271 $2p_o$=3.1351 $2p_1$=3.0623 $2s'$=3.9364 3s=1.1100	Ne Ne^+ Ne^{+2}	-127.721386 -127.371498 -126.049487	-127.488323 -126.522897 -124.572000
1s=9.6249 2s=2.9796 $2p_o$=2.3530 $2p_1$=2.2803 $2p'_o$=4.7946 $2p'_1$ = 4.8040 3s=1.1240	Ne Ne^+ Ne^{+2}	-128.508478 -127.816026 -126.302225	-127.935249 -126.775506 -124.745901

41

Table 9. Diatom Results: Exponents optimized to Ne

BASIS SET	ATOM /ION	GROUND STATE ENERGY	ONE 3S EXCITATION
1s=9.6414 2s=2.8870 $2p_o$=2.8800 $2p_1$=2.8801 3s=0.7930	Ne	-127.81404	-127.420756
1s=9.2722 2s=2.9507 $2p_o$=2.8775 $2p_1$=2.8774 $1s'$=14.9581 3s=0.7920	Ne	-127.86285	-127.477965
1s=9.7316 2s=3.1909 $2p_o$=2.8736 $2p_1$=2.8725 $2s'$=3.9143 3s=0.7920	Ne	-127.822468	-127.448297
1s=9.6322 2s=2.8817 $2p_o$=1.9915 $2p_1$=1.9751 $2p_o'$=4.5843 $2p_1'$=4.5325 3s=0.8110	Ne	-128.564608	-127.928911

42

Table 10. Diatom Results: Exponents optimized to Ne^{+2}

BASIS SET	ATOM /ION	GROUND STATE ENERGY	ONE 3S EXCITATION
$1s=9.6289$ $2s=3.0675$ $2p_o=3.2514$ $2p_1=3.3077$ $3s=1.3849$	Ne^{+2}	-126.088451	-124.726128
$1s=9.2450$ $2s=3.1680$ $2p_o=3.2491$ $2p_1=3.3072$ $1s'=14.9505$ $3s=1.3750$	Ne^{+2}	-126.156178	-124.808434
$1s=9.7264$ $2s=3.5025$ $2p_o=3.2664$ $2p_1=3.3248$ $2s'=4.0211$ $3s=1.3790$	Ne^{+2}	-126.117712	-124.778852
$1s=9.6228$ $2s=3.0560$ $2p_o=2.3028$ $2p_1=2.3977$ $2p_o'=4.3990$ $2p_1'=4.4048$ $3s=1.3819$	Ne^{+2}	-126.3273401	-124.866537

43

Appendix B. *Fitting Slater Functions to Gaussian Curves*

One of the approaches used to find the optimum Slater parameters for Diatom was to maximize the overlap integral of the Slater function with Gaussian functions, using Gaussian exponents from the literature.[4,14-17]

In most cases these Gaussian basis orbitals were sums of primitive Gaussian functions. The Gaussian functions are added together to better approximate true orbitals which have Slater function character. Matching Slater functions to Gaussian functions which are known to give good results should provide reasonable exponents to begin Diatom calculations.

With normalized functions a perfect match would produce an overlap integral value of unity. The overlap integral is evaluated by multiplying the two functions together and integrating over all space.

Another technique uses difference integrals which minimizes the integral of the absolute value of the difference between the two functions over all space. The difference integrals seemed to give better results when looking at plots of the two curves, because they looked closer together. When actually substituting the Slater parameters into Diatom the exponents that maximized the overlap integral gave better results sometimes, and the difference integral was better other times.

Figures 14 through 18 illustrate these results. Figure 14 shows a fit to a 1s orbital from the STO-3G basis set.[17] This was a test case which agreed with Szabo and Ostlund's result by finding 1 to be the best Slater exponent.[18]

Figures 15 and 16 illustrate the difference between the two curve fitting approaches in matching the 6-311G** 1s Neon atomic orbital. Figure 17 shows a 2s orbital fit illustrating some of the difficulties in matching Gaussian functions. Some Gaussian functions do not approximate Slater type orbitals. Finally, Figure 18 is a fit to a 6-21G Neon 2p orbital.

Even in the cases where Slater functions were matched to contracted Gaussians very closely, significant optimization of the parameters with Diatom was required. This approach also consumed a lot of time. Starting with Slater exponents in the literature proved much more useful, though they were more difficult to find, since most computational work uses Gaussian functions.

Overlap integral dependance on $\S$, the slater parameter
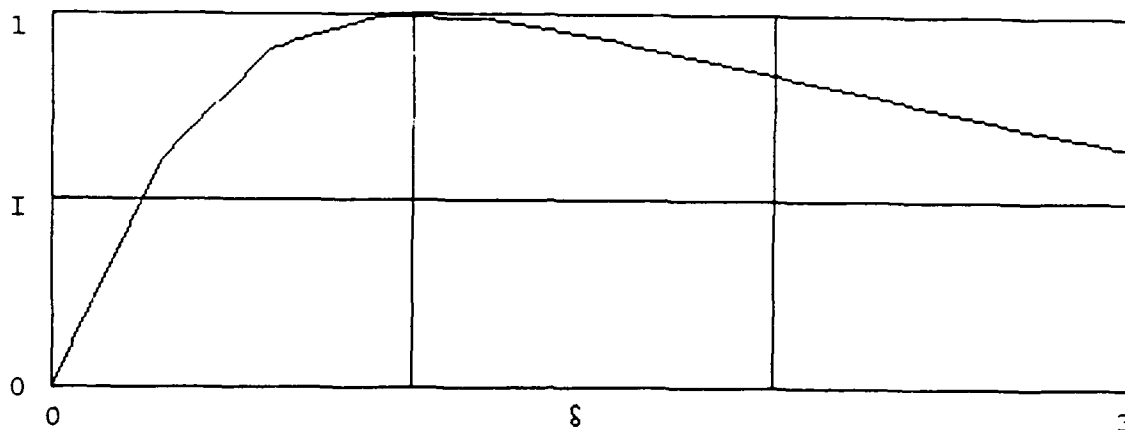
Slater fit to 1s gaussian:
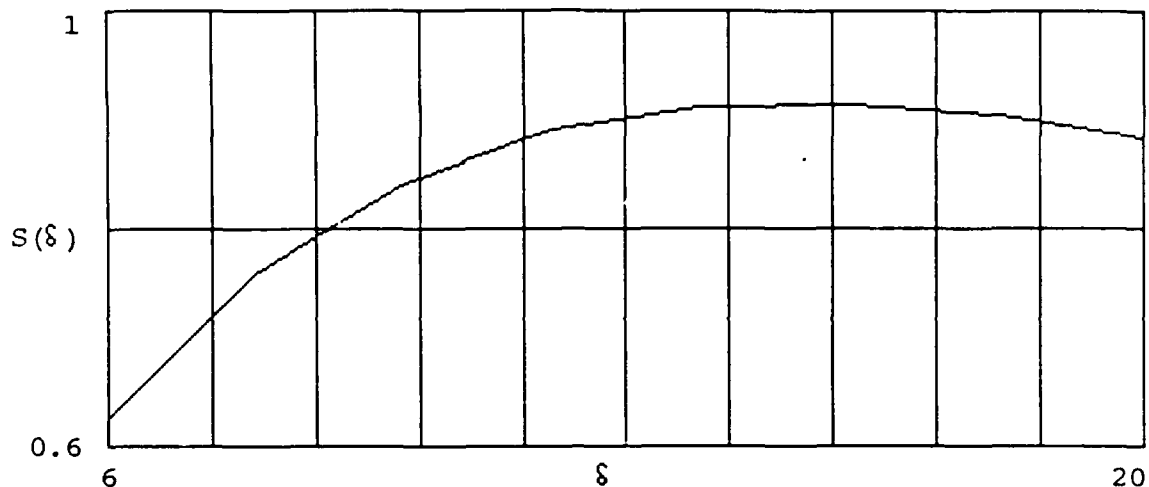## (The lower, more rounded curve is gaussian.)
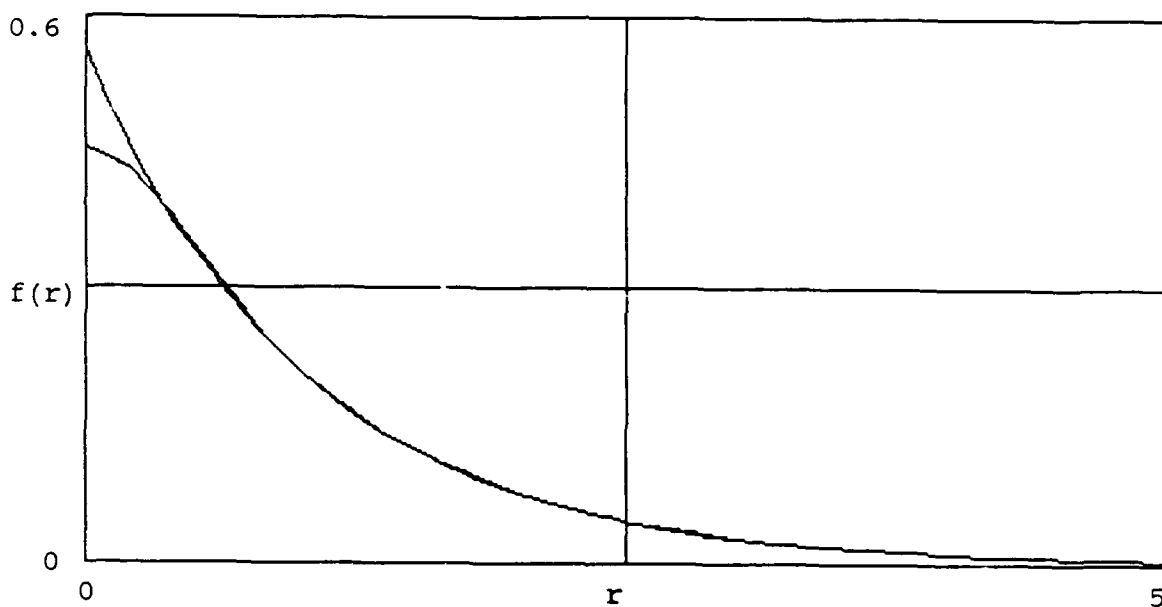
Figure 14. Overlap Integral Curve Fit to STO-3G for 1s Orbital: The top curve shows the value of the overlap integral as the Slater parameter varies from 0 to 2. As expected the maximum is at 1. The bottom plot shows the radial dependence of the resulting Slater function and the orthogonal Gaussian STO-3G function it was fit to. Slater and Gaussian functions are normalized so that their integral over all space is one.

Overlap integral dependance on δ, the slater parameter

Slater fit to NE 1s gaussian:
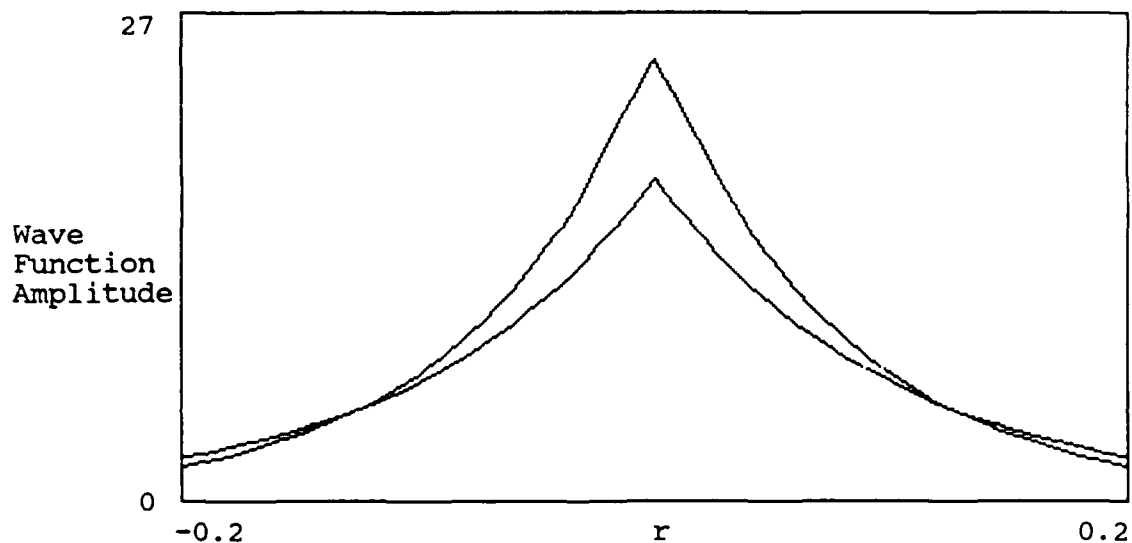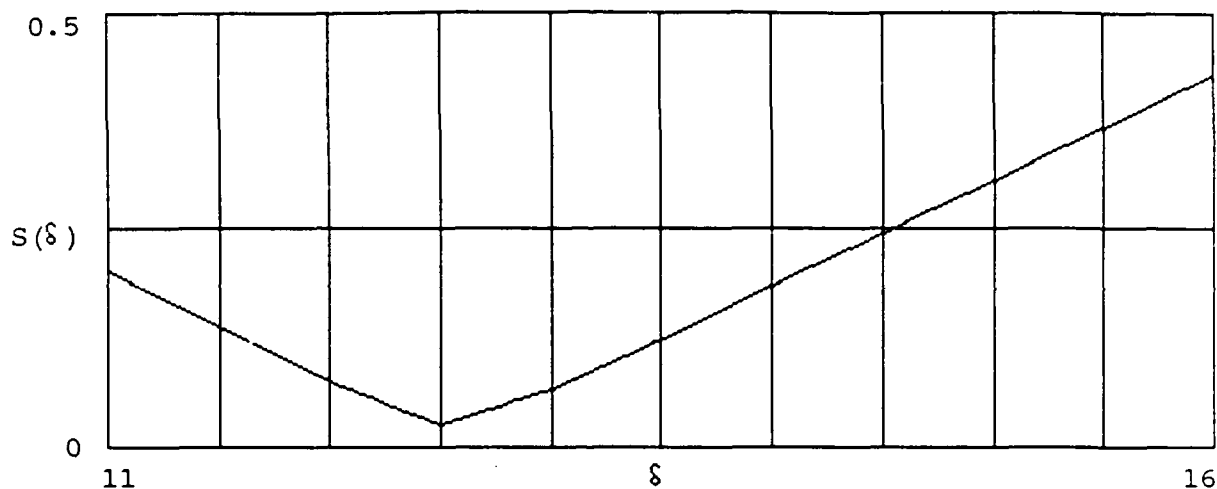(The upper, more rounded curve is Gaussian.)

Figure 15.   Slater Functions Fit to 6-311G** Gaussian for Neon 1s Orbital Using Overlap Integral: The top curve shows the overlap integral dependence on the Slater parameter which has a maximum at 15.26. The bottom curve shows the radial dependence of the Slater function and the 6-311G** Gaussian 1s function.

Difference Integral Dependence on δ, the Slater Parameter

Slater fit to NE 1s Gaussian:
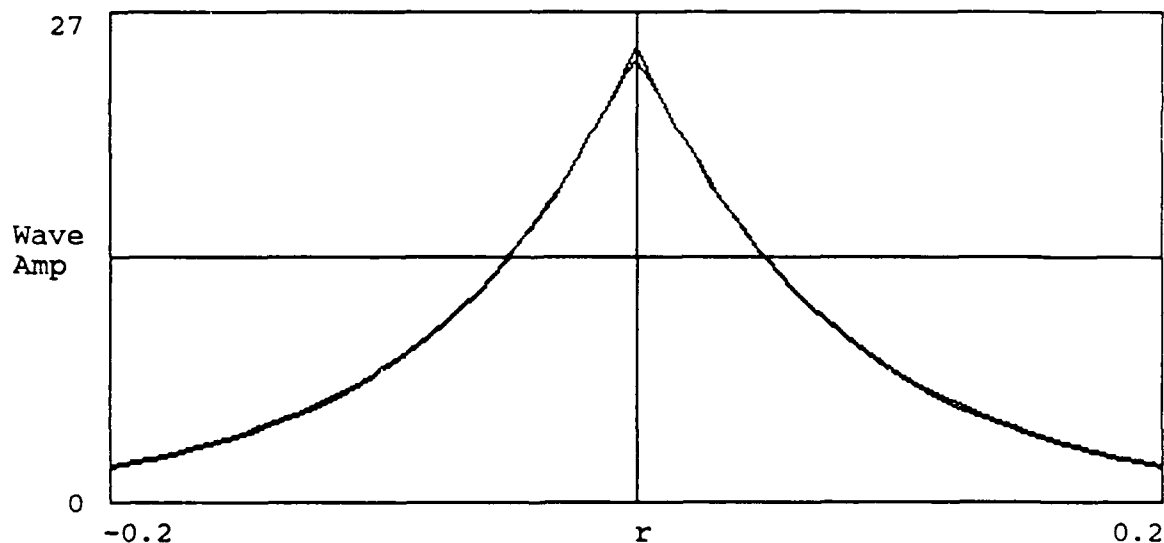## (The lower, more rounded curve is Gaussian.)

Figure 16. Slater Function Fit to 6-311G** Gaussian for Neon 1s Orbital Using the Difference Integral: The top curve shows the difference integral dependance on the Slater parameter, which has a maximum at 12.57. The bottom curve shows the radial dependence of the Slater function and the 6-311G** Gaussian 1s function.

Overlap integral dependence on δ, the Slater parameter
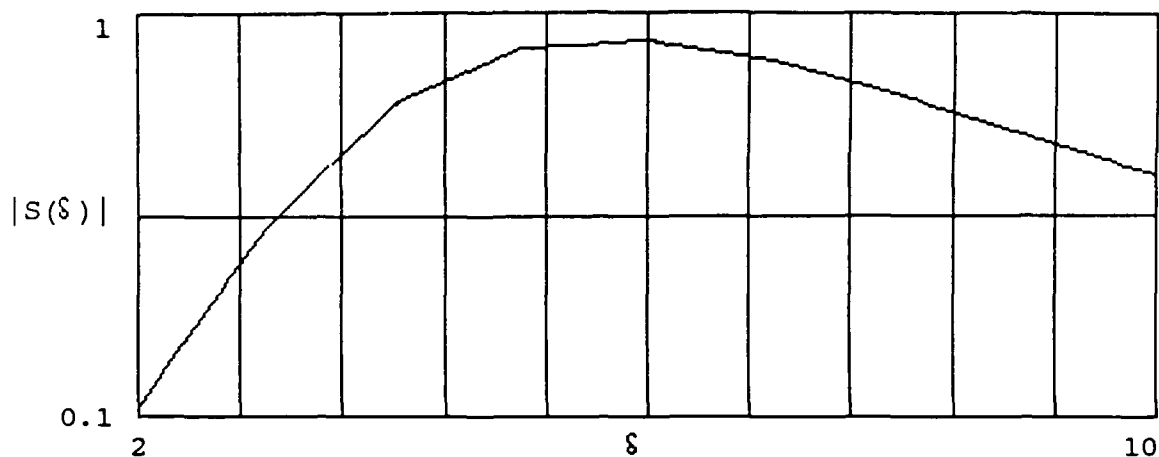
Slater fit to Ne 2s Gaussian:
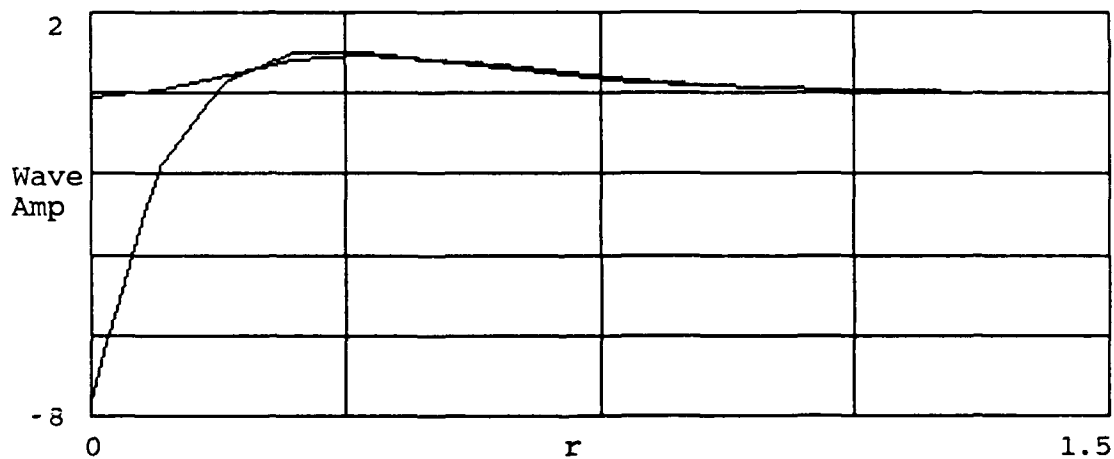(The sharp curve that peaks lower is the Slater function.)
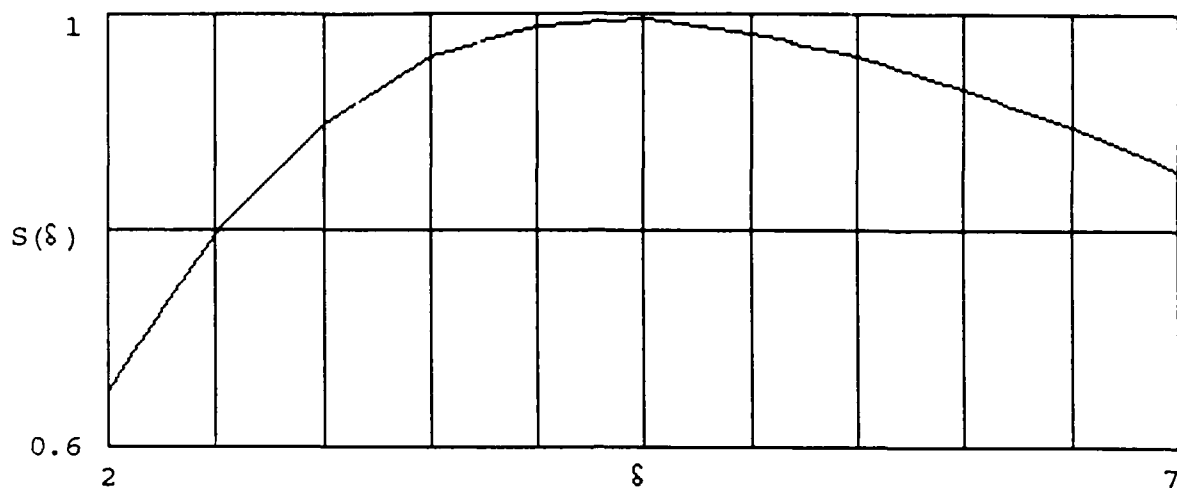

Figure 17. Slater Function Fit to 6-21G Gaussian for Neon 2s Orbital: The top curve shows the overlap integral dependence on the Slater parameter which has a maximum at 5.675. The bottom curve shows the radial dependence of the Slater function and the 6-21G Gaussian 2s function. You can see that this is a very poor fit. This was the best match achieved for the 2s orbital.

49

Overlap Integral Dependence on δ, the Slater Parameter

Slater function fit to Ne 2p Gaussian:
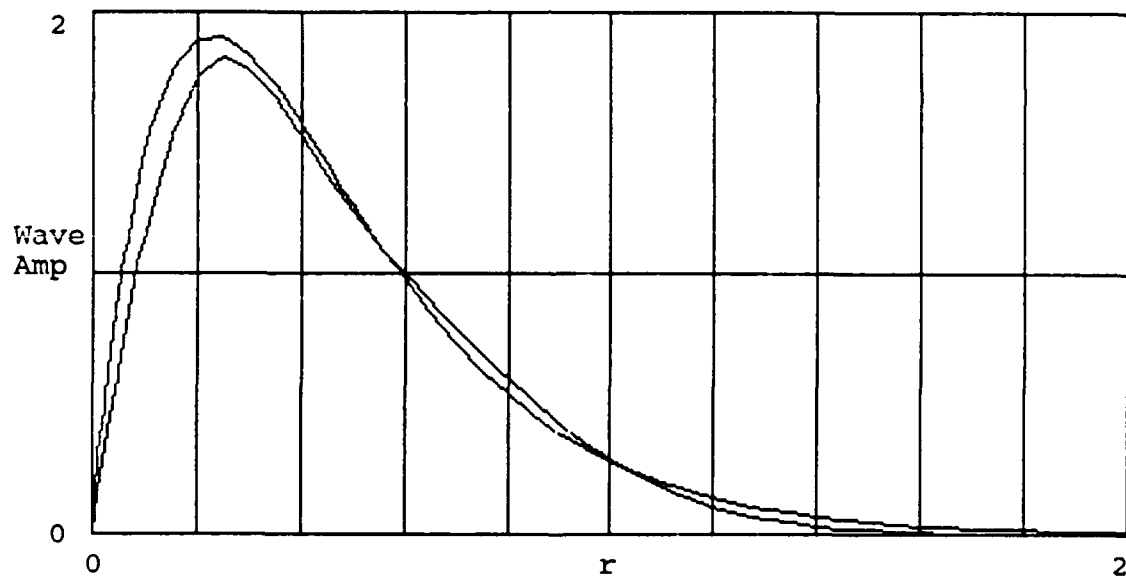## (The curve with a lower peak is Gaussian.)

Figure 18. Slater Function Fit to 6-21G Gaussian for Neon 2p Orbital: The top curve shows the overlap integral dependence on the Slater exponent which has a maximum at 4.3965. The bottom curve shows the radial dependence of the Slater function and the 6-21G Gaussian 2p function.

Appendix C. *Derivation of Induced Dipole Attractive Force*

At distances sufficiently large the Ne^{+2} ion can be treated as a point charge with a spherically symmetric electric field, E, pointing out in all directions,

$$E(r) = \frac{q}{4\pi\epsilon_0 r^2}$$

where q is the charge, which is 2e in this case, ϵ_o is the dielectric constant, and r is distance from the point charge.

This electric field induces a polarization, P, on Neon atoms,

$$P(r) = \alpha E(r), \quad \alpha = \text{polarizability}$$

which is parallel to, and in the same direction, as E. The Neon atom takes on a dipole charge which has the potential energy, U, in the electric field.

$$U(r) = -P(r)E(r) = -\alpha E^2 = \frac{-[\alpha q^2]}{16\pi^2\epsilon_o^2 r^4}$$

The fact that potential is proportional to $\frac{-1}{r^4}$ dictates that there must be a force acting to decrease r, the distance between the ion and the atom. As the two particles approach each other the potential energy decreases. The magnitude of th.. attractive force can be found simply by taking the derivative of the potential with respect to r.

$$F(r) = \frac{d}{dr}U(r) = \frac{4\alpha q^2}{16\pi^2\epsilon_o^2 r^5} = \frac{\alpha e^2}{\pi^2\epsilon_o^2 r^5}$$
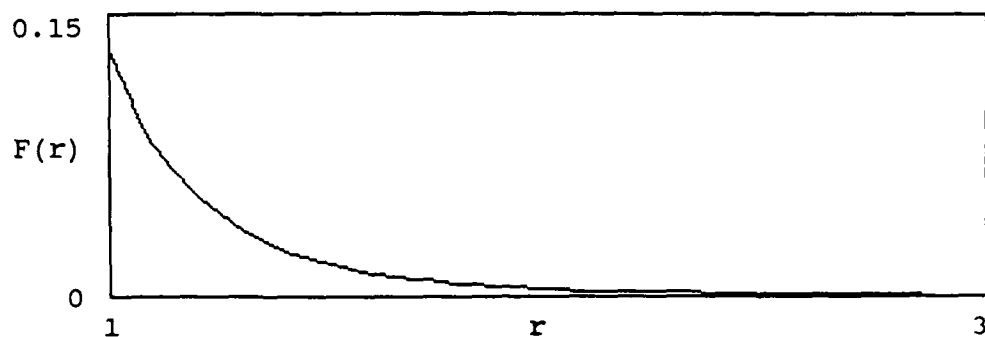
Figure 19. Induced Dipole Force: This plot shows the attractive force between a Neon atom and a doubly charged Neon ion due to the induced dipole. This force dominated at nuclear separations large enough to neglect core repulsion.

In the case at hand $e = 1.602 \times 10^{-19} C$, $\epsilon_o = 8.854 \times 10^{-12} C/Vm$ and $\alpha = 3.96 \times 10^{-4} nm^3$.

Substituting into the force equation one finds the attractive force between the ion and atom to be:

$$F(r) = \frac{0.13138}{r^5} V^2 nm^5$$

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[19]Vibrational levels were computed using BASIC software developed by Steven E. Koonin. A Lennard-Jones potential was used which roughly approximated the $^3\Sigma$ upper level data with a = 3.5 a.u. and V_o = 0.029943 a.u. resulting in gamma = 116. The Lennard-Jones fit was a conservative one. It was steeper than the actual data, so that the true potential well would have more than the 21 bound vibrational modes computed.

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This research computed Neon dimer dication potential energies for nuclear separations from 0.9 to 20 a.u. of Ne_2^{+2}. Sigma, pi, and delta states are considered which dissociate to two Ne^+ atoms in their ground state, or to the Ne atom and Ne^{+2} ion in their ground states. The purpose of examining these characteristics is to demonstrate that the charge transfer reaction is primarily radiative.

$$Ne^{+2} + Ne \rightarrow Ne^+ + Ne^+ + h\nu$$

Electronic structure calculations indicate that Ne^{+2} should bind with Ne to form Ne_2^{+2*}. Once the molecule relaxes by collisions with third particles it should remain in this bound state near 4 a.u. nuclear separation until it can transition to the lower level by radiative charge transfer. Such a process would emit electromagnetic radiation with 0.677 a.u. (18.43 eV) energy.

The ground state is shown to be dissociative over the entire range of nuclear separations considered, a beneficial condition of excimer laser media.

Results for a Helium test case are also presented. Atomic Helium's first 8 energy levels were calculated to within a few mili-Hartrees (mH) of experimentally determined values. Energy surfaces for He_2^{+2} agreed with Cohen and Bardsley's[1] results to within a few mH.