

3.2: Time Scale Separation

The physical parameters that determine under what circumstances the BO approximation is accurate relate to the motional time scales of the electronic and vibrational/rotational coordinates.

The range of accuracy of this separation can be understood by considering the differences in time scales that relate to electronic motions and nuclear motions under ordinary circumstances. In most atoms and molecules, the electrons orbit the nuclei at speeds much in excess of even the fastest nuclear motions (the vibrations). As a result, the electrons can adjust 'quickly' to the slow motions of the nuclei. This means it should be possible to develop a model in which the electrons 'follow' smoothly as the nuclei vibrate and rotate.

This picture is that described by the BO approximation. Of course, one should expect large corrections to such a model for electronic states in which 'loosely held' electrons exist. For example, in molecular Rydberg states and in anions, where the outer valence electrons are bound by a fraction of an electron volt, the natural orbit frequencies of these electrons are not much faster (if at all) than vibrational frequencies. In such cases, significant breakdown of the BO picture is to be expected.

This page titled [3.2: Time Scale Separation](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Jack Simons](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.